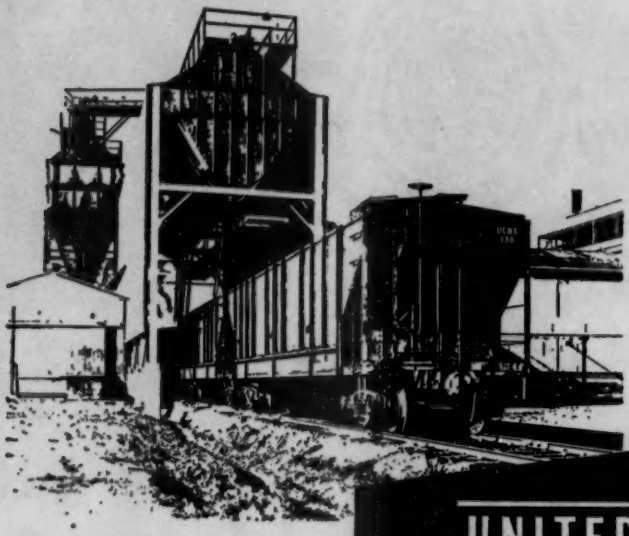
JULY - SEPTEMBER • 1959

VOLUME XXXII • NUMBER THREE

RUBBER CHEMISTRY AND TECHNOLOGY

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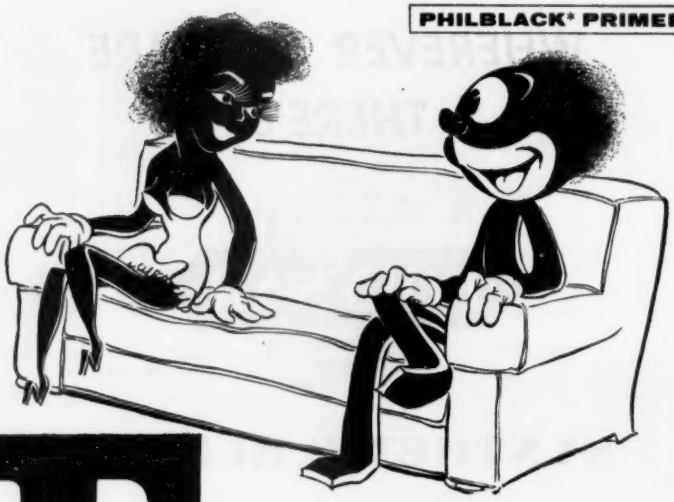
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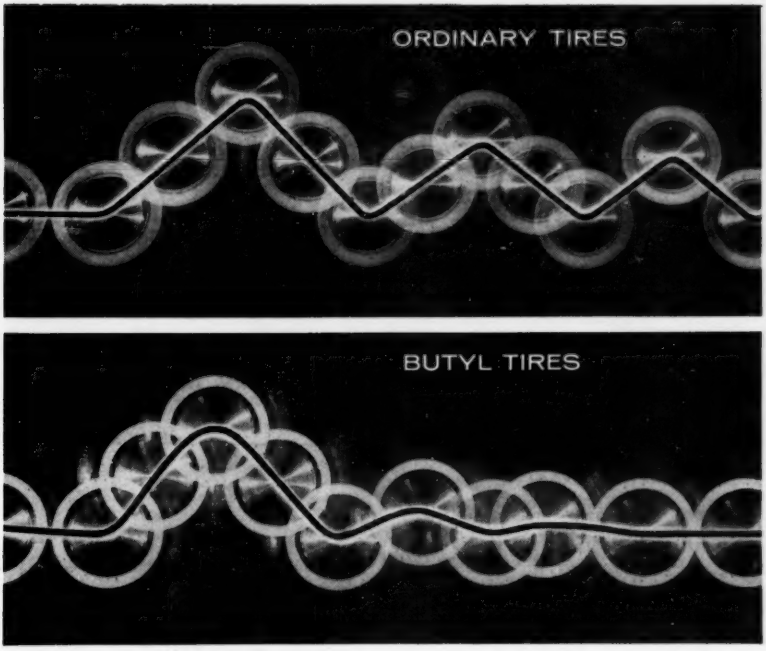
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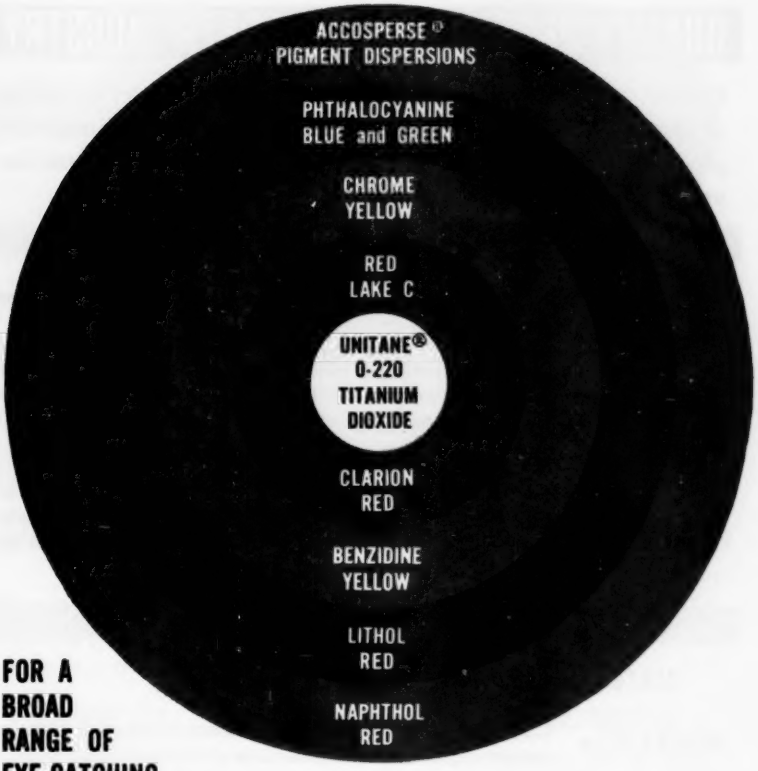
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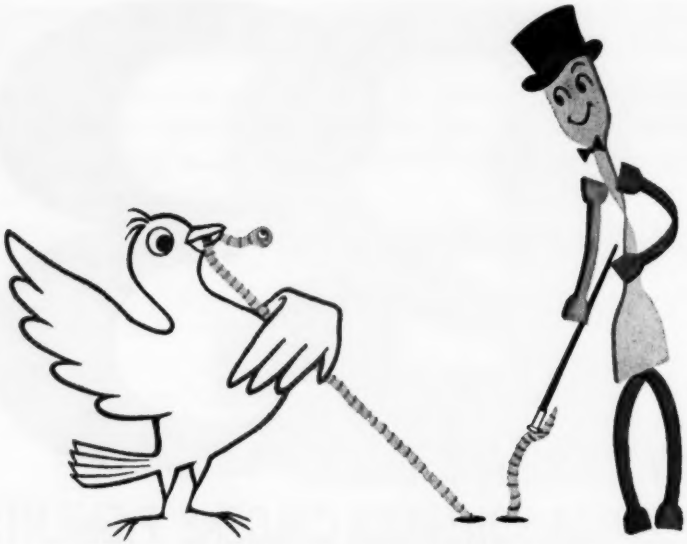
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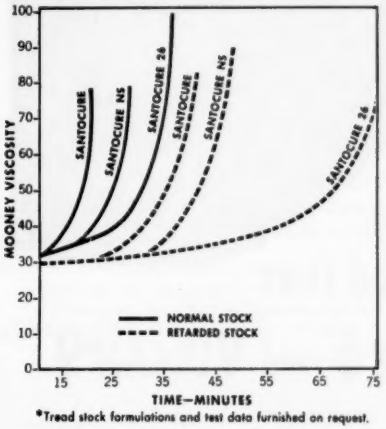
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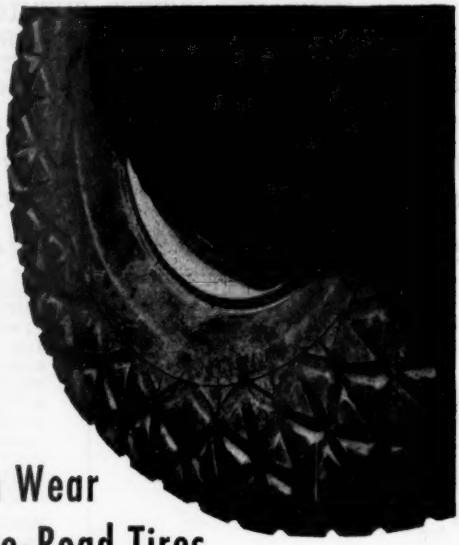
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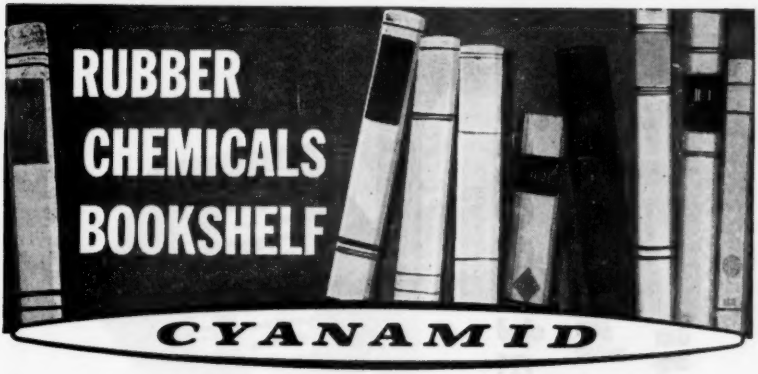
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Vulcan 6 Intermediate Super Abrasion Furnace Black
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GUANIDINES DPG and DOTG
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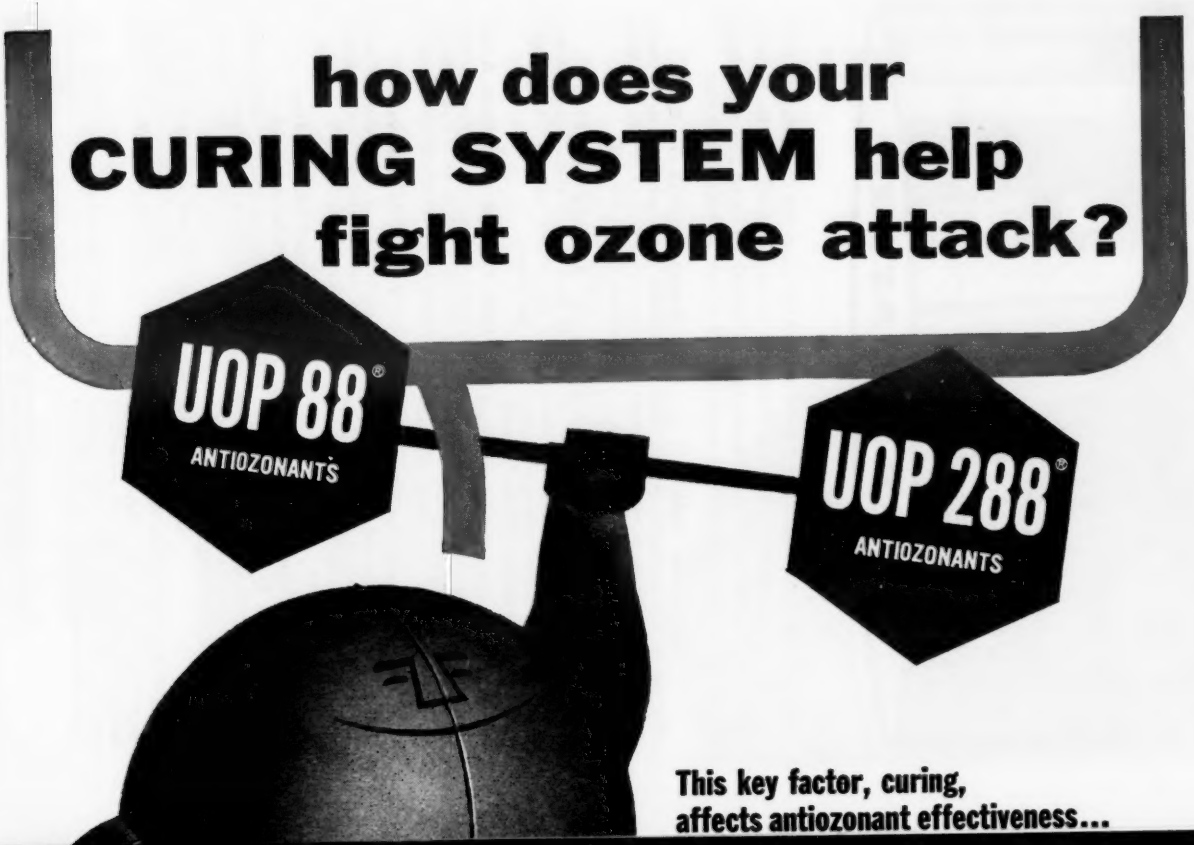
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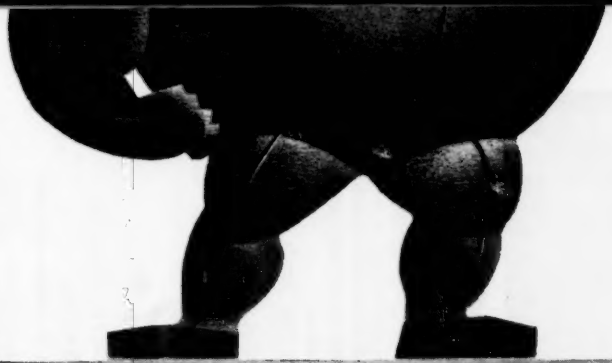
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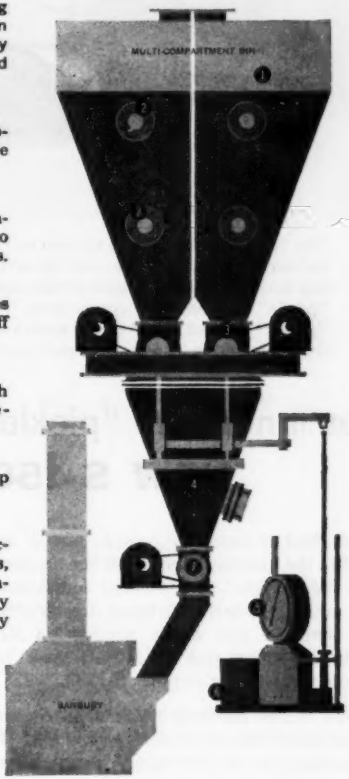
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Meeting		City	Hotel	Date
1959	Fall	Washington*	Shoreham	November 9–13
1960	Spring	Buffalo	Statler	May 3–6
1960	Fall	New York	Commodore	Aug 28–Sept 3
1961	Spring	Louisville	Brown	April 18–21
1961	Fall	Chicago	Sherman	September 5–8
1962	Spring	Boston	Statler	May 15–18
1962	Fall	Philadelphia	—	September 11–14
1963	Spring	Toronto	Royal York	May 7–10
1963	Fall	New York	Commodore	September 10–13
1964	Spring	Detroit	Cadillac	April 28–May 1
1964	Fall	Chicago	Sherman	September 1–4

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Chairman: CHARLES H. KUHN (Master Processing Corp., Lynwood). *Assoc. Chairman:* B. R. SNYDER (R. T. Vanderbilt Co., Los Angeles). *Vice-Chairman:* W. M. ANDERSON. *Secretary:* C. M. CHURCHILL (Naugatuck Chemical, East Los Angeles). *Asst. Secretary:* EDMUND J. LYNCH (H. M. Royal, Inc., Downey, Calif.). *Treasurer:* HOWARD R. FISHER (W. J. Voit Rubber Co., Los Angeles). *Directors:* ROY N. PHELAN (Atlas Sponge Rubber Co., Monrovia), WILLIAM J. HANEY (Kirkhill Rubber Co., Brea), JOHN L. RYAN (Shell Chemical Corp, Torrance), CARL E. HUXLEY (Enjay Co., Los Angeles), WALTER E. BOSWELL (Thiokol Chemical Corp.). Meetings in 1959: May 5, June 5, 6 and 7, October 6, November 3, December 11.

NEW YORK RUBBER GROUP

Chairman: R. B. CARROLL (R. E. Carroll, Inc., Trenton, N. J.). *Vice-Chairman:* E. S. KERN (R. T. Vanderbilt, 230 Park Ave., N. Y.). *Secretary-Treasurer:* R. G. SEAMAN (Rubber World, New York). Terms end December 31, 1959. Meetings in 1959: October 16, December 18 at Henry Hudson Hotel.

NORTHERN CALIFORNIA RUBBER GROUP

President: DRACE "KUT" KUTNEWSKY (Burke Rubber Co., San Jose). *Vice-President:* CLAUDE "CORKY" CORKADEL (Oliver Tire & Rubber Co., Oakland). *Treasurer:* JOE MATTSON (Witco Chemical Co., San Francisco). *Secretary:* RAY BROWN (Burke Rubber Co., San Jose). *Directors:* KEITH LARGE, VIC CARRIERE. Meetings in 1959: September 5, October 8, November 5, December 5.

Philadelphia Rubber Group

Chairman: R. S. Graff (E. I. du Pont de Nemours & Co., Wilmington). *Vice-Chairman:* H. C. Remsberg (Carlisle Tire & Rubber, Carlilse, Pa.). *Secretary-Treasurer:* R. N. Hendrickson (Phillips Chemical Co., 2595 East State Street, Trenton, N. J.). *Executive Committee:* T. E. Farrell, R. N. Hendriksen, James Jones, George N. McNamara, J. R. Mills, H. M. Sellers, Merrill Smith. *National Dir.:* M. A. Youker (E. I. du Pont de Nemours & Co., Wilmington). Meetings in 1959: May 1, August 21, October 2 (Poor Richard Club), November 6 (Dance for members only).

Rhode Island Rubber Group

Chairman: H. W. Day (E. I. du Pont de Nemours & Co., Boston). *Vice-Chairman:* Harry L. Ebert (Firestone, Fall River, Mass.). *Secretary-Treasurer:* W. J. Blecharczyk. *Historian:* R. G. Bolkman (U. S. Rubber Co., Providence). *Executive Committee:* E. S. Uhlig, R. B. Robitaille, J. M. Vitale, C. A. Damicone, G. E. Enser. Meetings in 1959: June 12–14, November 5, Pawtucket Country Club, Pawtucket, R. I.

Southern Ohio Rubber Group

Chairman: R. J. Hoskin (Inland Mfg. Div., Dayton, Ohio). *Chairman-Elect:* F. W. Gage (Dayton Chem. Products Labs., West Alexandria, Ohio). *Treasurer:* J. M. Kelble (Wright Patterson AF Base, Ohio). *Secretary:* R. E. Wells (Precision Rubber Prod. Co., Dayton 17, Ohio). *National Director:* F. W. Gage (Dayton Chem. Products Labs., West Alexandria, Ohio). Meetings in 1959: October 8, December 12.

Southern Rubber Group

Chairman: Warren Hall (Phillips Chemical Co., 318 Water Street, Akron, Ohio). *Vice-Chairman:* E. H. Ruch (Firestone Tire and Rubber Co., Memphis, Tenn.). *Secretary:* E. Strube (E. I. du Pont de Nemours and Co., Atlanta, Ga.). *Treasurer:* R. C. Whitmore (Better Monkey Grip Co., Dallas, Texas). Meeting in 1959: Oct. 9 and 10 Peabody Hotel, Memphis, Tenn. Meeting in 1960: Feb. 12 and 13 Shamrock Hilton Hotel, Houston, Texas.

Washington Rubber Group

President: Robert Stiehler (National Bureau of Standards). *Vice-President:* A. W. Sloan (Atlantic Research, Alexandria, Va.). *Secretary:* George T. Richey (National Bureau of Standards). *Treasurer:* J. R. Britt (B. F. Goodrich Co.). *National Director:* A. W. Sloan. Meetings in 1959: April 6, May 4, Patomac Electric Power Co. Auditorium.

Ontario Rubber Group

Chairman: O. R. Huggenberger (Dominion Rubber Co. Ltd., Montreal).

NEW BOOKS AND OTHER PUBLICATIONS

1958 Book of ASTM Standards—Part 9: Plastics, Electrical Insulation, Rubber, Carbon Black. Published by the American Society for Testing Materials, 1916 Race Street, Philadelphia 3, Pennsylvania. Hard cover, 6 ×9¼ inches, 2018 pages. Price: $14.00.—The Book of ASTM Standards is a triennial publication with supplements issued in the intervening years. It contains the formally adopted ASTM Standards and Tentative Specifications, Methods of Test, and Definitions. The 1958 edition comprises over 13,500 pages and has been issued in ten parts. Part 9 contains the specifications and methods of test for rubber and carbon black among other materials.

The section on rubber, which occupies some 675 pages, is divided into parts on the following: Processibility Tests, Chemical Tests, Physical Tests, Aging and Weathering Tests, Low Temperature Tests, Automotive and Aeronautical Rubber, Packing and Gasket Materials, Hose and Belting, Tape, Electrical Protective Equipment, Rubber-Coated Fabrics, Insulated Wire and Cable, Hard Rubber, Latex Foam, Sponge and Expanded Cellular Rubber, Rubber Adhesives, Crude Rubber, Rubber Latex, Synthetic Elastomers, Rubber Compounding Materials, and Electrical Tests.

The section on carbon black contains parts on chemical tests, physical tests and on an optical test.

The physical layout of the book meets all the requisites which one demands of such an encyclopedic volume. The standards are assembled in a sequence determined by the specific materials or products to which they apply. The type is clear, the paper of good quality, and the diagrams, illustrations and tables readily legible. The table of contents is presented in two parts—one a list of the standards classified according to the materials covered, the other, printed, on colored stock, a list of the standards in numeric sequence of their serial designations. A subject index of the standards and tentatives in the volume appears at the back.

The Society has maintained the standard of editorial craftsmanship and thoroughness which it has achieved in similar volumes in the past. It is to be congratulated on the continuing high quality of its endeavors. [Reviewed in *Rubber Age* (N. Y.).]

Fundamentals of High Polymers. By O. A. Battista. Published by Reinhold Publishing Corporation, 430 Park Avenue, New York 22, New York. Hard cover, 6¼ × 9¼ inches, 140 pages. Price: $5.00.—This book has been written to serve as an introductory textbook for courses in high polymers at the undergraduate level. For that reason a broad spectrum of high polymer technology is served providing a bird's-eye view of the field, but the relation of high polymers to industry is also discussed in regard to commercially important applications. To meet the needs of the beginner in the field, a generous supply of schematic diagrams has been included.

The first chapter of the book is devoted to the best definitions available for key terms of high polymer science. The author felt this chapter particularly necessary because of the ambiguity and confusion which currently exists as to the exact meanings of certain terms used in the field.

The book is divided into two parts. Part I, "Basic Principles of High Polymers", has in addition to the chapter on basic definitions one other on the chemistry of high polymers. Part II, "Formation of Products from Macromolecules", is comprised of the following chapters: "The Building Blocks of

High Polymers", "Macromolecules in Solution", "The Solid State of High Polymers", "Physical Properties of High Polymers", and "The Future of High Polymers". The book closes with a bibliography and subject index.

The bibliography, which lists 89 references, is divided into lists of various subjects, with the appropriate references under each heading. The groupings are: Adhesives, Biochemistry, Cellulose, Chemistry, Copolymerization, Fibers, Physical Properties, Physics, Plastics, Polyamides, Polyethylene, Polymerization Proteins, Resins, Rubbers, Silicones and General High Polymer Textbooks. Eight of the references pertain to rubber.

Besides its function as a basic textbook, this volume will serve as a handy reference for chemists, engineers, and others interested in academic or industrial research on high polymer technology. Others in nontechnical capacities may also find the book useful as a means of familiarizing themselves with the fundamentals of the science on which high polymer products are based. [Reviewed in *Rubber Age* (N. Y.).]

KUNSTSTOFF-, LACK- UND GUMMI-ANALYSE. By Dieter Hummel. Published by Carl Hanser Zeitschriftenverlag GmbH., Leonhard-Eck-Strasse 7, Munich 27, Germany. Volume I. 409 pages, 19 figures, 26 tables. Volume II. 548 infrared spectra. Price: 148 DM (about $35.00).—The excellent thesis of these twin volumes is that the best tools for identifying polymers, copolymers, and auxiliaries used in commercial plastics, resins, finishes, and synthetic rubbers is a combination of infrared with chemical color tests, together with some knowledge of the types of products being manufactured. The authors have brought together in concise and well-organized form the information from the scattered literature in German and English relating to identification of high polymers and auxiliaries as they occur in commercial products; moreover Volume II is an excellent collection of infrared spectra obtained at Stuttgart using the Perkin-Elmer 21 instrument (2 to 15 microns). Few German polymer books have included such complete coverage of publications in Britain and America.

The first 76 pages of Volume I discuss methods of preparing samples for chemical and IR tests, documentation of results, physical methods, and chemical group reactions. Pages 77 to 316 treat under chemical types of polymers and methods for "wet analyses" together with discussion of the most significant IR absorption maxima (referring to Volume II for the complete spectra). The polymer types and their derivatives include the following, with the number of different IR spectra given in Volume II: Natural Resins (19); Drying Oils, Waxes, and Rosin Derivatives (45); Cellulose Derivatives (9); Asphalts, etc. (6); Phenolic Resins (53); Hydrocarbon Polymers (48); Halogen-Containing Polymers (19); Ester Polymers (59); Ether Polymers (31); Nitrogen-Containing Polymers (43); Silicon-Containing Polymers (7); Plasticizers (68); Stabilizers, Vulcanizing Agents, and Other Auxiliaries (50). Volume I includes references to 30 books and almost 700 journal articles. Spectra of a number of intermediates and of a few monomers, obtained by pyrolysis of polymers, are also given. With most of the spectra are given trade-names, manufacturer, chemical composition, and method of preparing the sample.

Interest in these books should extend beyond the strictly analytical, since Hummel discusses structural problems and includes a number of German copolymers and derivatives which are not well known. However, the absence of some acrylic and vinyl ester copolymer products of Germany and the United States is noted. The book even includes some eutactic polymers, such as

polypropylene plastics, but gives little about copolymer emulsion finishes, or about high impact plastics modified by rubbery copolymers which have become important in America. Among the few weak sections of Volume I is that on solubility and identification of poylvinyl alcohols. A limited amount of useful information on compositions might have been included from selected patents. [Reviewed by C. E. Schildknecht in *Journal of Polymer Science.*]

RUBBER. By Ir. A. van Rossem. Published by Servire, The Hague, Holland. 6 × 9¼ inches, 170 pages. Price: f8.90 (about $2.32).—(In Dutch.) Dr. van Rossem, retired professor of the Technical University of Delft, former director of the Netherlands Government Rubber Institute for more than 30 years, and former director of the Research Department of the Rubber Foundation at Delft, is undoubtedly one of the world's authorities on the subject of rubber.

The author says in his preface that it would have been easier for him to write a book two or three times the volume of the present one, but, nevertheless, he has succeeded in his own careful way in writing a very complete treatise on the subject in a small volume. Although technology of natural rubber forms the backbone, a fair amount of space is given to the synthetic elastomers.

The 170 pages are divided into 12 chapters: "History", "Plantation", "Latex", "Chemical Compositions", "Physical Properties", "Processing", "Vulcanization", "Manufacturing Using Dry Rubber Processing", "Manufacture of Articles from Latex", "Properties of Vulcanizates as a Function of the Composition of Mixes", "Durability, Statistical" and "Economical Considerations". Twenty-three photographic and over forty printed illustrations are in the text. A list of reference books is also added.

This excellent little book gives as thorough and clear a story as can be condensed in a volume of this size. The author mentions in the preface that the book can be handled by anyone with a complete high school background, except for the passages on the chemistry of rubber. This may be somewhat optimistic in some respects, but anybody reading this book with interest will enjoy it and benefit. [Reviewed by B. B. Boonstra in *Rubber Age* (N. Y.).]

GUM PLASTICS (RUBBER-MODIFIED PLASTICS). By M. S. Thompson. Published by Reinhold Publishing Corporation, 430 Park Avenue, New York 22, New York. Hard cover, 5 × 7½ inches, 194 pages. Price: $4.50.—This book is the ninth in a series currently being offered by the publisher devoted to guidance and application of the increasing number of plastics materials. The author gives a general introduction to the field of gum plastics, and follows with extended chapters on general properties of these products, basic chemistry and manufacture, processing and fabrication, and commercial applications.

The book centers around impact-polystyrene polymers, ABS (acrylonitrile-butadiene-styrene) polymers, and impact-rigid polyvinyl chloride polymers, chosen because they are more important commercial polymers. Extensive treatment has been given to their applications and to the reasons for their use. The chapters on general properties, chemistry, and fabrication techniques have been written so as to provide a more fundamental understanding of these compounds and how best to apply them.

In the past decade the class of materials combining plastics and rubber has achieved great commercial significance. A summary glance of the extensive list of applications given by the author—they range from refrigerators to industrial pipe—makes one instantly aware of the import of these materials on

the rubber industry. For this basic reason the volume is an important one, perhaps even more so for the people connected with rubber and with plastics in a non-technical capacity than for the scientist.

The book presents an excellent over-all survey of gum plastics, their history, production and uses. A reader can acquire an excellent general knowledge of the field by studying its contents, and also a basic understanding of the technology of these plastics. The author has done a scholarly job, and is to be commended for his competent survey of a widely diversified industry. [Reviewed in *Rubber Age* (N. Y.).]

SOVIET RUBBER TECHNOLOGY. A cover-to-cover translation of the monthly *Kauchuk i Rezina* (Raw Rubber and Compounded or Cured Rubber), a periodical of the State Committee on Chemistry of the U.S.S.R. Council of Ministers. The translating and publishing are produced under the auspices of the Department of Scientific and Industrial Research Translations Unit, and in collaboration with Maclaren and Sons, Ltd., Maclaren House, 131 Great Suffolk Street, London S. E. 1, England, by the Research Association of British Rubber Manufacturers. Price per year in U. S. A. $50.00. The Foreword by W. F. Watson in the first issue states:

"The emergence of the Soviet Union as a first-class scientific power and as a prolific source of original literature has posed a serious problem to the Western nations in that comparatively few of their nationals can read Russian, and it is therefore very difficult for them to follow technical progress being made there. In particular, it has been obvious in recent years that Soviet rubber technology and research is very vigorous and highly advanced.

"It will be our aim to follow up this issue by translating each number of the Russian original, as it appears, with the minimum of delay, in a dignified, readable and technically sound version, and to make it available at a reasonable price to the Western world. No doubt there will be difficulties but these must be overcome, as we cannot afford to remain in even partial ignorance of what is being done in technology in the Soviet Union.

"The translator and editor, Mr. M. Lambert, is on the staff of the Research Association of British Rubber Manufacturers."

The table of contents of the first issue is as follows, the original *Kauchuk i Rezina* page number being in parenthesis:

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The translation retains the volume and issue numbers of *Kauchuk i Rezina*. The printing is superior to the original Russian and the figures are at least as clear. The journal in translation ($8\frac{1}{8}$ inches by $10\frac{1}{4}$ inches) is approximately the same size as *Kauchuk i Rezina*. The Research Association of British Rubber Manufacturers is to be congratulated for undertaking this truly important task.

CHARLES GOODYEAR MEDAL AWARD FOR 1960

To all members of the Division of Rubber Chemistry:

This letter is for the purpose of soliciting proposals for candidates for the Charles Goodyear Medal Award for consideration by the Medal Committee at the Fall meeting to be held in Washington, D. C., November 9–13, 1959.

Your proposals should be presented in the form suggested in the *Outline for Proposal* given below, and mailed to the Division Secretary, Dr. R. H. Gerke, so as to reach him not later than Sept. 15.

For your guidance, I am listing below the past Goodyear Medalists and also a list of fields not yet fully recognized. Additional awards in fields already recognized, e.g., polymerization and vulcanization, are, of course, in order. The by-laws do not prohibit the election of a foreign technologist.

I hope that each of you will consider this matter carefully.

E. H. Krismann, Chairman
Charles Goodyear Medal Committee

OUTLINE FOR PROPOSAL OF A CANDIDATE

FOR THE

CHARLES GOODYEAR MEDAL AWARD

1. Name of candidate.....
2. Statement of contribution of candidate for use for the Award Citation...
3. General statement concerning the importance of such contribution.....
4. Pertinent publications of the candidate.....
5. Brief biography of the candidate.....
6. Name, address, and signature of proposer member of the Division of Rubber Chemistry

Fields Not Yet Fully Recognized

Among fields which have not been fully recognized may be mentioned: Physics of rubber, including kinetic theory, dynamic and electrical properties; reinforcement; oxidation; antioxidants; polychloroprene (neoprene); vulcanizable copolymers of isobutylene and dienes (butyl); cold SBR and oil-extended SBR; polyacrylate rubber; silicone rubber; isocyanate rubbers; reclaiming; delayed-action accelerators; new reinforcing fillers; new processing equipment.

Charles Goodyear Medalists

1941 David Spence. A pioneer of rubber chemistry, who did much important early work. No lecture given.

1942 L. B. Sebrell. Research on antioxidants and accelerators. Lecture: "The Second Mile", *Industrial and Engineering Chemistry*, **1943**, p. 736; Rubber Chemistry and Technology, **1943**, p. 713.

1944 W. L. Semon. Synthetic rubber research. Lecture: "Research leading to commercial butadiene synthetic rubber", *Chemical and Engineering News*, **1946**, p. 2900; *India Rubber World*, **1946**, p. 364.

1946 Ira Williams. Neoprene and overall accomplishments. Lecture: "Vulcanization of rubber with sulfur", *Industrial and Engineering Chemistry*, **1947**, p. 901.

1948 George Oenslager. Pioneer in organic accelerators. No lecture given.

1949 H. L. Fisher. Long in the field of rubber chemistry; overall accomplishments. Lecture: "Rubber research and the need for a rubber research institute in the United States".

1950 C. C. Davis. Development of the oxygen bomb test for accelerated aging; *Chemical Abstracts*; Rubber Chemistry and Technology; Editor "The Chemistry and Technology of Rubber". Lecture: "Some of the real pioneers of the rubber industry", *India Rubber World*, **1951**, p. 433.

1951 W. C. Geer. Oven aging test, de-icer for airplanes, encouragement of rubber research. Lecture: "Strategy in rubber research", *Industrial and Engineering Chemistry*, **1951**, p. 2436.

1952 H. E. Simmons. One of the early and best known teachers of rubber chemistry, and an inspirational guidance of younger men. Lecture: "Out of the past".

1953 J. T. Blake. Research on oxidation and vulcanization. Co-editor of "The Chemistry and Technology of Rubber". Accumulative accomplishments. Lecture: "The future of rubber", *Chemical and Engineering News*, **1953**, p. 4290.

1954 G. S. Whitby. Research on plantation rubber, vulcanization, accelerators, GR-S synthesis, overall accomplishments. Editor of "Synthetic Rubber". Lecture "Reflections on rubber research", *Industrial and Engineering Chemistry*, **1955**, p. 806.

1955 R. P. Dinsmore. Numerous important contributions to rubber chemistry and technology; recipient of honors. Lecture: "Specifications for a rubber chemist", *Rubber World*, **1956**, p. 57.

1956 S. M. Cadwell. Contributions to the field of rubber chemicals and to the control of vulcanization. Lecture: "Scientific Contributions to the Rubber Industry".

1957 A. W. Carpenter. For his many contributions to the testing of rubber and rubber products. Lecture: "The Tower of Babel", *Rubber World*, **1957**, p. 241.

1958 J. C. Patrick. For the discovery, development and vulcanization of Thiokol polysulfide polymers. Lecture: "Comments on the Polysulfide Polymers".

EFFECT OF PRIMARY MOLECULAR WEIGHT ON THE DYNAMIC PROPERTIES OF CURED RUBBER *

E. V. Kuvshinskiĭ and M. M. Fomicheva

All-Union Scientific Research Institute for Synthetic Rubber, Leningrad, USSR

During studies of the dependence of the mechanical properties of vulcanized rubber on the primary molecular weight of the original rubber, basic attention has been given to strength characteristics[1–7]. Dynamic properties have been investigated only in passing. Usually only rebound elasticity has been determined with the use of the pendulum-type Schob elastometer. In the experiments in which a more advanced method of investigation was applied, the data indicated that the dependence of dynamic properties on the molecular weight of the original rubber is mostly qualitative.

As known, the dynamic modulus of resilience and the elasticity of the vulcanized rubber changes with the degree of vulcanization. In the majority of experiments only the "optimal" vulcanizates, that is, the ones giving the best strength characteristics, were subjected to studies. The condition of the vulcanizing network in these experiments was not controlled in any way.

In a more basic manner were studied types of vulcanized rubber containing carbon black. The addition of carbon black noticeably evened out the influence of the basic structural peculiarities of natural rubber.

The purpose of our research was to bring to light the influence of the molecular weight through comparison of the properties of vulcanized rubber samples made from different vulcanization processes, distinctive in magnitude of pseudo-equilibrium modulus of resilience[1]. This value defines the elastic stresses remaining in the vulcanized specimens which have been under 15% compression for 1.0 hour at a temperature of 60° C. The pseudoequilibrium modulus of resilience appears to be a measure of the crosslink density.

It follows from References 8 to 9 for unfilled vulcanized rubber specimens prepared from the same raw rubber that the variation in the mechanical and dynamic properties resulting from changes in processing and by conditions of vulcanization (within definite limits) is related to the change in the pseudo-equilibrium modulus of elasticity with sufficient consistency.

The vulcanized stocks were prepared as for styrene-butadiene rubber, SKS-30-A. The accelerators of the vulcanization with sulfur were diphenylguanidine (DPG), mercaptobenzothiazole (MBT) and triethanolamine. The composition of the mixtures is given in Table I.

The dynamic and mechanical characteristics of the vulcanized rubber (rebound elasticity and dynamic modulus) were determined on the pendulum type elastometer KC with 0.02–0.04 second duration of impact at temperatures of 20, 60, and 100° C.

The initial raw rubber and its thermoplasticate were separated into fractions by fractional precipitation. The characteristic viscosity of the fractions and their molecular weights are given in Table II.

* Translated from *Zhur. Tekh. Fiz.* **27**, 1019–1028 (1957).

TABLE I

Ingredients \ Recipe no.	1	2	3
Natural rubber	100	100	100
Sulfur	2	2	3
DPG	1.5	—	—
Triethanolamine	—	4	—
MBT	—	—	1
Magnesium oxide	5	10	—
Zinc oxide	—	—	5
Stearic acid	1	1	1

The mixing of the raw rubber with the ingredients on a micromill under generally accepted regimes of mixing caused extensive degradation of the rubber. The changing of the molecular weight during the mixing process was negligible only for the fractions and unfractionated raw rubbers whose molecular weights were below 150,000 (Table III). An increase in temperature and decrease of mixing time did not prevent degradation of the rubber. Therefore the preparation of rubber compounds was carried out by addition of the ingredients to solutions of rubber in benzene followed by evaporation[6].

The resulting sheets (films) were rolled up into rolls and were cured for a short time period in press molds. The specimens had the form of cylindrical plugs with a diameter of 10 mm and a height of 10 mm. After having been tested for mechanical properties the specimens were additionally cured by heating in a thermostat at the same cure temperature and tested again. In order to reach a greater degree of vulcanization the dosage of sulfur in the series of specimens was doubled. The total time of vulcanization did not exceed 3–4 hours. During this period the processes connected with degradation could not significantly distort the general picture of the variation of properties due to vulcanization. Using this method we could conduct a sufficiently complete investigation of properties of rubbers, while using small amounts of the fractions.

The general laws of variation of properties of vulcanized rubber with temperature and degree of vulcanization as determined by us are in agreement with the results of Reference 9. The pseudoequilibrium modulus increases with the rise in degree of vulcanization, reaching in some isolated cases the values of 70–80 kg/cm^2.

The dynamic modulus of elasticity of the raw rubber at 20° C was sufficiently high and equal to 20 kg/cm^2, and at 100° C—13.5 kg/cm^2. It is slightly sensitive to increase in crosslink density (Table IV).

TABLE II

CHARACTERISTIC VISCOSITIES (η) AND MOLECULAR WEIGHTS M OF THE FRACTIONS OF STYRENE–BUTADIENE RUBBER "SKS-30-A" AND ITS THERMOPLASTICATE

No.	[η]	M	No.	[η]	M
1	5.52	840,000	9	1.38	116,000
2	4.44	622,000	10*	1.12	86,000
3	3.72	485,000	11*	1.06	80,000
4	2.64	294,000	12*	1.03	76,000
5	2.55	280,000	13*	0.96	69,000
6*	2.42	260,000	14	0.71	45,000
7*	1.58	141,000	15*	0.57	33,000
8*	1.52	133,000	16*	0.54	30,000

* The starred fractions are extracts of plasticates obtained by thermo-oxidative degradation.

TABLE III

VARIATION OF MOLECULAR WEIGHT OF STYRENE–BUTADIENE RUBBER "SKS-30-A" AFTER MILL MIXING AT 60° C (MIXTURE NO. 2)

		Polymer SKS-30-A						
		Defoe hardness				Fraction SKS-30-A		
		2800 g			660 g			
		Mixing time						
		15 min	15 min	30 min	15 min	15 min	15 min	15 min
Molecular weight, M	before mixing	4.56×10^5	4.56×10^5	4.56×10^5	1.35×10^5	8.40×10^5	2.93×10^5	8.70×10^4
	after mixing	2.56×10^5	2.41×10^5	2.37×10^5	1.21×10^5	3.05×10^5	2.33×10^5	7.65×10^4
Change in molecular weight, %		43	47	48	10	64	20	12

During the vulcanization as the pseudoequilibrium modulus increased by 3.5–4 times, the change in the dynamic modulus of elasticity was negligible. With an increase in temperature the dynamic modulus decreases, but always remains greater than the pseudoequilibrium modulus. This decrease in the dynamic modulus with the increase in temperature becomes more pronounced with lower concentration of crosslinks. At higher degrees of vulcanization the dynamic modulus becomes equal to the pseudoequilibrium modulus. The rate of approaching to each other of the values of the dynamic and pseudoequilibrium modulus becomes higher in proportion to the increase in the temperature of testing of the dynamic modulus. The manner of increase of the dynamic modulus for a given degree of cure depends on the type of accelerator. When MBT is used the modulus increases more smoothly than is the case with triethanolamine. The dynamic modulus of elasticity is little dependent on the molecular weight of the initial natural rubber. Only in the vicinity of molecular weight lower than 100,000 there may be noticed some decrease in its value (Figure 5). Evidently, the dynamic resilience of vulcanized rubber is conditioned, in the first place, by the presence of sufficiently frequent physical junc-

TABLE IV

DYNAMIC MODULI OF ELASTICITY OF VULCANIZED RUBBER AT DIFFERENT TEMPERATURES *

Pseudo-equilibrium modulus, kg/cm²	Accelerator	Dynamic modulus at temperatures		
		20° C	60° C	100° C
10	Triethanolamine	45	32	28
20	Triethanolamine	47	35	31
35	Triethanolamine	48	40	38
10	MBT	30	30	23
20	MBT	40	34	30
40	MBT	47	42	40

* The values of dynamic modulus were badly reproduced in parallel specimens. The divergence in separate cases reached 15%. Therefore Table IV gives the mean values of moduli obtained from three parallel specimens.

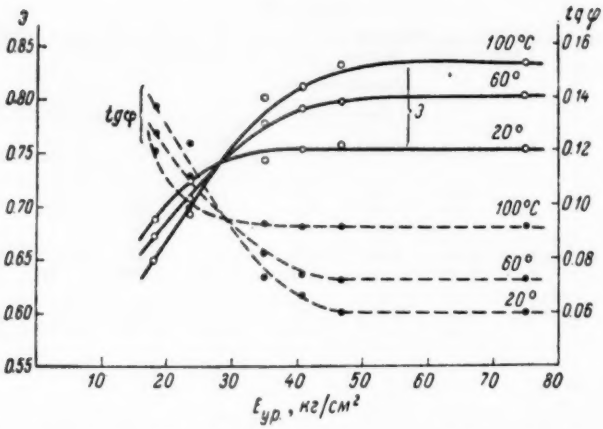


FIG. 1.—Dependence of rebound elasticity (э) and tangent of the angle of dynamic losses (tan φ) on the pseudoequilibrium modulus ($E_{ур}$), kg/cm², at different temperatures. Accelerator: DPG.

tions (that is, interlocking of the polymer chains with each other, and also of sections with strong local intermolecular interaction) which limit the freedom of movement of the macromolecules in fixed intervals in the same manner as is accomplished by strong crosslinks formed as a result of chemical interaction. Only at high temperatures, at high degrees of vulcanization, and at low deformation rates does the presence of a chemical crosslink network have a predominant effect.

With an increase in the degree of vulcanization the rebound elasticity increases to some limit. At low degrees of vulcanization the rebound elasticity falls off with an increase in temperature, and at high degrees—it increases. In Figure 1 are shown values for a vulcanized rubber made from a fraction with a molecular weight of 133,000 and vulcanized with varying additions of sulfur (from 1 to 8 parts) in the presence of diphenylguanidine. In the same figure is shown the dependence of the tangent of the angle of mechanical losses on the conditional equilibrium modulus related to the elasticity on the rebound э by the equation

$$\tan \varphi = \frac{1}{\pi} \ln \frac{1}{э} = 0.73 \lg \frac{1}{э}$$

The vulcanized rubbers which contained the accelerator triethanolamine lent themselves to detailed study (Figure 2).

The simplest laws are valid at 100° C. At this temperature all points fall on the same common curve. Some tendency for points to fall below the general curve is noticed only for vulcanized rubbers made from fractions with a molecular weight of 45,000 (Figure 2, *a*). At 60° C the relationship between the rebound elasticity and the pseudoequilibrium modulus is given by several gradually increasing curves (Figure 2, *b*) which correspond to the different molecular weights of fractions from which the rubbers were obtained. In this manner with a decrease of temperature the dependence of elasticity on the molecular weight becomes evident. The strongest dependence of elasticity on the

molecular weight is observed at a temperature of 20° C. In this case it may be seen (Figure 2, *c*) that the greater the molecular weight, the greater the limiting importance of elasticity which may be obtained with a sufficiently high density of the spatial vulcanization net. If we compare the variation of elasticity with temperature, as was done in Figure 1 we can establish that with the increase of molecular weight of a fraction the change in the sign of the temperature dependent coefficient of elasticity will take place in vulcanized rubbers with high values of the conditional equilibrium modulus at high values of elasticity (Figure 3).

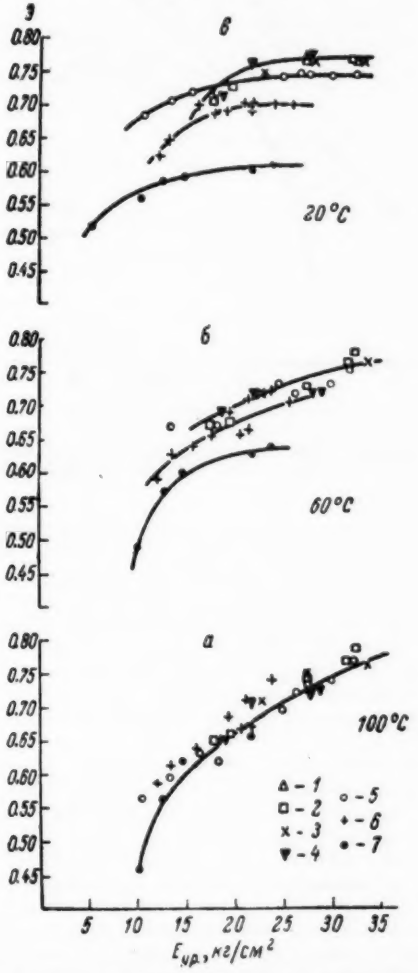


FIG. 2.—The dependence of rebound elasticity on pseudoequilibrium modulus at various temperatures. Accelerator: triethanolamine.

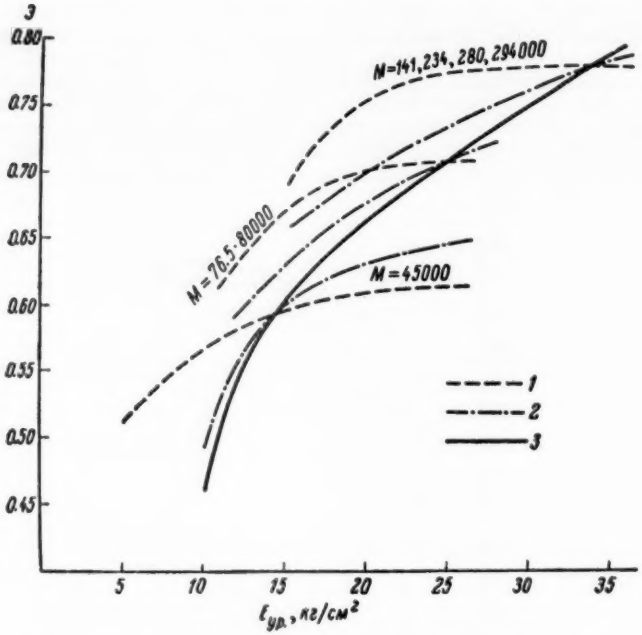


FIG. 3.—Dependence of the rebound elasticity on the pseudoequilibrium modulus at various temperatures. Accelerator: triethanolamine.

Thus, for vulcanized rubbers obtained from fractions with $M = 45{,}000$ the corresponding value of the pseudoequilibrium modulus is 15 kg/cm², for $M \geqq 141{,}000$ it will reach 34 kg/cm², and the elasticity increases from 0.59 to 0.77. For vulcanized rubbers made in the presence of DPG and MBT all the above rules are analogous. The only distinction consisted of the following: in vulcanized rubbers made with DPG the increase of rebound elasticity with the pseudoequilibrium modulus takes place at the slowest rate, the intermediate position is occupied by the vulcanized rubber made with triethanolamine, and the highest rate of increase of rebound elasticity is found in the stocks made with MBT (Figure 4).

The maximum value of the rebound elasticity of vulcanized rubber at 20° C with a given molecular weight of the initial rubber is not dependent on the type of accelerator. This maximum elasticity for vulcanized rubbers with different accelerators arises at different values of the pseudoequilibrium modulus. Thus for fractions with a molecular weight of 133,000 the rebound elasticity ceases to change for values of the pseudoequilibrium modulus above 24 kg/cm² for vulcanized rubbers with MBT, 28 kg/cm² for those with ethanolamine, and 40 kg/cm² for those with diphenylguanidine. Such differences in the critical values of the pseudoequilibrium modulus is possibly connected with differences in the characteristics of the crosslinks and their different spatial arrangement.

On the basis of the data on the dynámic and mechanical properties and their connection with the pseudoequilibrium modulus of vulcanized rubber it is possible to study the dependence of the change of properties of the vulcanized rubber on the molecular weight of the raw rubber at any given phase of vulcanization. When the pseudoequilibrium modulus of vulcanized rubber made from a fraction of any molecular weight equals 25 kg/cm^2 then the rebound elasticity at 20° C reaches its limiting maximum value. From the technical point of view this degree of vulcanization corresponds to overcure. At such values of the pseudoequilibrium modulus the region of noticeable dependence of rebound elasticity on molecular weight starts at $M \leqq 100{,}000$ (Figure 5).

A complete independence of the elasticity from the initial molecular weight is reached at molecular weights above 150,000. At a psuedoequilibrium modulus equal to 15 kg/cm^2 the region of a strong dependence of elasticity on the molecular weight is displaced towards somewhat higher molecular weights.

Until this time in order to ascertain the influence of the molecular weight we compared properties of vulcanized rubbers having equal values of equilibrium modulus (that is, with the same number of crosslinks). Another method of comparison is possible, aimed at the determination of the influence of the molecular weight of the natural rubber on the properties of vulcanized rubber containing an equal number of sulfur bridges. By sulfur bridge is meant an atom or group of atoms of sulfur which connects the molecules of natural rubber, ir-

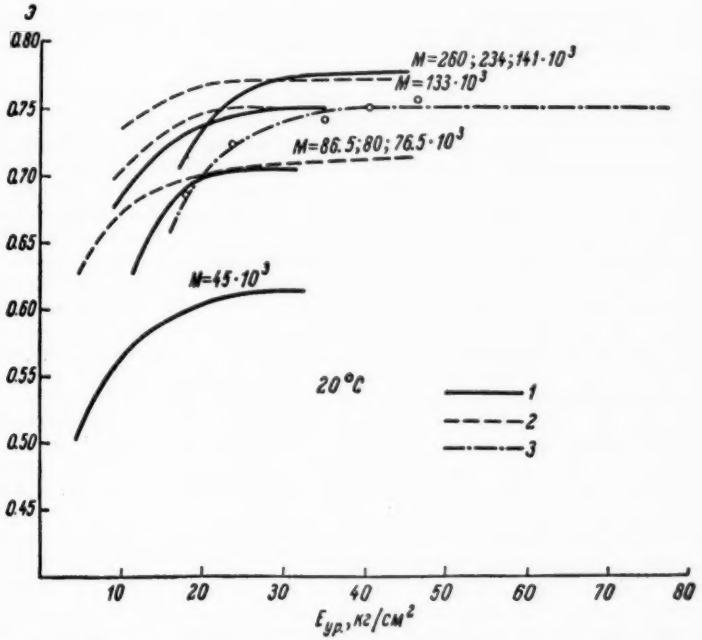


FIG. 4.—Dependence of rebound elasticity on the pseudoequilibrium modulus of vulcanized rubber, with different accelerators; ——— triethyanolamine; - - - - - MBT; - · - · - DPG.

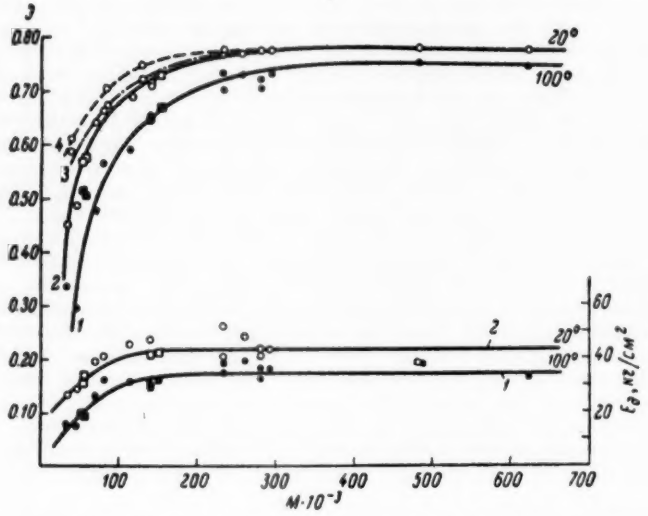


FIG. 5.—Dependence of elasticity and dynamic modulus on the molecular weight at 20° C (circles) and 100° C (solid circles). *1* and *2*—$E_{yp} < 10$ kg/cm²; *3*—$E_{yp} = 15$ kg/cm²; *4*—$E_{yp} = 20$ kg/cm²; empty squares—vulcanized rubbers made from a mixture of fractions.

respective of whether a spatial net is formed, or whether the crosslink atom brought about only an extension or branching out of the molecule. It follows from Reference 6 that in some cases the rate of joining of sulfur is independent of the molecular weight of the natural rubber. Thus rubber vulcanized during equal intervals of time from fractions with different molecular weights should contain an equal number of sulfur bridges. In this case the influence of the molecular weight of the initial raw rubber should show up first of all in that in vulcanized rubbers made from low-molecular fractions with an equal number of sulfur bridges only a small part of the bridges become effective junctions of a spatial net, and the greater part of the bridges connect the separate molecules without intensifying the network. In high molecular weight fractions almost every such bridge should also be a junction in the net. To our regret it turned out that in our case the low molecular weight fractions, obtained from the thermoplasticate, joined sulfur to themselves at a high rate. (Free sulfur was determined by the method of Bolotnikow[10] altered in "NIIRP" for application to small batches of vulcanized rubber.) Therefore, the comparison of the properties of vulcanized rubbers, vulcanized under the same conditions was not completely self consistent. We will limit ourselves to giving the data related to the very first phases of vulcanization, because they complement the experimental material quoted (in these vulcanized rubbers the psuedoequilibrium modulus of elasticity was less than 10 kg/cm², Curves *1* and *2* of Figure 5). It follows from Curve *1* in Figure 5 that at a low degree of vulcanization the elasticity ceases to be dependent on the molecular weight for values of $M \geqq 200{,}000$. At 100° C the magnitude of the limiting maximum elasticity decreases in its absolute value and the region of dependence of elasticity on the molecular weight becomes wider up to $M \geqq 300{,}000$ (Curve *2*).

TABLE V

MOLECULAR WEIGHTS OF FRACTIONS AND ESTIMATION OF M_v., M_η AND M_B OF MIXTURES OF FRACTIONS

Molecular weights of initial fractions	Ratio by weight	M_v.	M_η	M_B
622,000 + 30,000	17:3	155,000	507,000	532,000
485,000 + 30,000	41:8	141,000	375,000	417,000
622,000 + 30,000	12:13	55,000	256,000	314,000
485,000 + 30,000	51:49	57,000	220,000	262,000

In addition to vulcanizates prepared from fractions of various raw rubbers, mixtures of fractions were also studied. The composition of the mixtures is given in Table V.

The points which characterize the properties of vulcanized rubber made from mixtures of fractions fall on the appropriate curves if the mixtures are characterized by a mean value of molecular weight the behavior being very sensitive to the content of the low molecular weight fractions in the mixture[11].

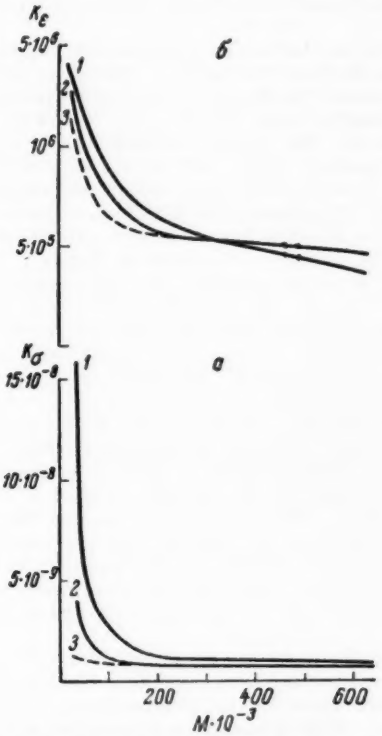


FIG. 6.—Dependence of the friction modulus and of specific loss taken to the second power of stress on the molecular weight. *1*—$E_{yp} < 10$ kg/cm², $t = 100°$ C; *2*—$E_{yp} < 10$ kg/cm², $t = 20°$ C; *3*—$E_{yp} = 25$ kg/cm², $t = 20°$ C.

Consequently, as far as the dynamic properties of vulcanized rubber are concerned the determining role is played by low molecular weight fractions, provided they are contained in the initial raw rubber in noticeable quantity.

The rebound elasticity defines the relative losses of energy during the impact compression and allows no possibility of judging the absolute magnitude of the heat generated. To this end, such characteristics as specific energy losses, taken to the second power of stress

$$\left(K_\sigma = \frac{\pi^2 (1 - \sqrt{\vartheta})}{2E_D (1 + \sqrt{\vartheta})}\right)$$

as well as the friction modulus

$$\left(K\epsilon = \frac{E_D}{2} \frac{1 - \vartheta}{\sqrt{\vartheta}}\right)^8$$

may be used. The impact losses of energy (calculated from the data of Figure 5) taken to the second power of stress, and the modulus of friction are given in Figures 6a and 6b.

From Figure 6 it may be seen that the absolute magnitude of loss falls off with the increase of the molecular weight of the initial rubber. The region of the greatest significance of the loss and of the highest rate of decrease is limited to the molecular weights below 150,000 in the case of the loss related to the second power of stress. The friction modulus changes more gradually under those conditions, becoming independent of the molecular weight near M = 200,000 at 20° C. At 100° C in the region of molecular weights between 300,000–400,000 the modulus of friction in the initial phases of vulcanization is lower than at 20° C which is connected, evidently, with the increase of elasticity caused by the increase in molecular weights (see Figure 5, Curve 4).

It follows from the rules obtained that the question of the influence of molecular weight of the raw rubber on the dynamic and mechanical properties of vulcanized rubber is closely connected with the question of the influence of the degree of vulcanization. Some considerations on the influence of vulcanization are expressed in Reference 9. The molecules of a polymer are connected to the network both by strong chemical bonds, and by weaker physical bonds whose number and stability fall off sharply with increase in temperature. Because of this the total number of the segments of chains which belong to the spatial net and give it elasticity decreases; and the number of chains which have lost their bond to the network, or, are still "connected" only by one end, increases correspondingly. The last (poorly connected chains) limit the motion of elastic elements and lower the elasticity at a low density of chemical crosslinks. On the other hand, the intervals of relaxation of segmental motion become lower when the temperature decreases, which causes an increase in elasticity at higher temperature in the case of a sufficient density of the chemical crosslinks.

The influence of the molecular weight, evidently, becomes evident in the defects in the network (after Flory), conditioned by the presence of free chain ends. It will be particularly high in vulcanized rubbers made from low molecular weight products. With an increase in temperature, as mentioned above, the general mobility of the chains increases, the free ends do not retard the motion of the chains during the impact deformation as much and at 100° C the elastic-

ity is defined totally by the density of the chemical crosslinks in the vulcanizate. The question on why the variation of the temperature coefficient of elasticity with the decrease of molecular weight takes place in the region of the lowest pseudoequilibrium modulus (Figure 3) remains open.

In conclusion the authors would like to express their gratitude to I. J. Poddubnyi, who helped us with his advice and direction during the development of this work.

CONCLUSIONS

1. Studied were the moduli of resilience and rebound elasticity of the vulcanized rubbers made from fractions of butadiene-styrene rubber "SKS-30-A" at temperatures of 20, 60, and 100° C in the region of molecular weights from 45,000 to 620,000 with various degrees of vulcanization (with variation in the pseudoequilibrium modulus from 5 to 70 kg/cm^2).

2. The dynamic modulus of resilience is little dependent on the molecular weight of the original rubber both at room temperature and at higher temperatures.

3. At higher temperatures the elasticity of vulcanized rubber is mainly determined by the degree of vulcanization, the measure of which is the pseudoequilibrium modulus, and is little dependent on the initial molecular weight. At low temperatures (20° C) elasticity increases with the degree of vulcanization, but it increases at different rates for vulcanized rubbers made from fractions with different molecular weights. At 20° C the increase in the degree of vulcanization increases the elasticity of vulcanized rubbers made from low-molecular fractions (45,000) to a lower degree than of those made from high molecular weight fractions (above 133,000).

4. The value of the maximum elasticity of vulcanized rubbers obtained from rubbers of the same molecular weight is not dependent on the type of accelerator used.

REFERENCES

[1] Flory, P. J., *Ind. Eng. Chem.* **38**, 417 (1946).
[2] Janko, J. A., *J. Polymer Sci.* **3**, 576 (1948).
[3] Johnson, B. L., *Ind. Eng. Chem.* **40**, 351 (1948).
[4] Beatty, J. R., and Zwicker, B. M. G., *Ind. Eng. Chem.* **44**, 742 (1952).
[5] Novikov, A. S., Chakina, M. V., Dorochina, T. B., and Archanhelskaya, M. Y., *Colloid Journal* **15**, No. 1, 51 (1953).
[6] Novikov, A. S., Bartenev, G. M., and Galyl-Ogly, F. A., *Doklady Akad. Nauk USSR* **94**, No. 2, 253 (1954).
[7] Poddubnyi, I. J., Reich, W. N., Starovoitova, E. I., and Nazarov, V. H., Account of WNYYSK, 1953.
[8] Kuvshinskil, E. V., and Sidorovycz, E. A., *Zhur. Tekh. Fiz.* **26**, 879 (1956).
[9] Kuvshinskil, E. V., and Sidorovycz, E. A., *Zhur. Tekh. Fiz.* **27**, 702 (1957) ; see following paper, this issue.
[10] Bolotnikov, W., and Gurova, W., *Journal of R. P.* **10**, No. 6, 61 (1933).
[11] Marei, A. I., Altshuler, M. Z., and Fomicheva, M. M., Account of WNYYSK, No. 128, 1950.

EFFECT OF VULCANIZATION ON THE DYNAMIC PROPERTIES OF RUBBER *

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It is a known fact that the mechanical properties of rubber depend essentially upon the density (i.e., the crosslink density) of the vulcanization network. The dependence of the "equilibrium" (statistical) modulus of elasticity upon the concentration of crosslinks as well as the dependence of the tensile strength —has been studied in a series of investigations[1–5]. In contrast to this, analogous investigations of the dynamic mechanical characteristics[6] are practically nonexistent. We have undertaken our present work with the hope of filling this gap.

Series of gum compounds were prepared from natural (smoked sheet) and synthetic polyisoprene (SKI), sodium butadiene (SKB), butadiene-styrene (SKS-30A), and butadiene-nitrile (SKN-26) rubbers which varied in their degree of vulcanization. The percentage of sulfur and accelerator were varied as were the temperature and the time of vulcanization. The mechanical-dynamic characteristics of the rubber at a predetermined impact pressure—the rebound elasticity and the dynamic elastic modulus were studied[7] with the pendulum elastometer KS over a temperature range of 20–100° C. The duration of the stress was .03/.05 second.

We estimated the concentration of crosslinks in the rubber samples from the magnitude of the equilibrium modulus. In order to determine this characteristic, we compressed specimens which were 20 mm in height and 10 mm in diameter 15% and studied the relaxation of stress. The specimens were also tested on the pendulum elastometer. Heppler's consistometer operating on the lever weight principle, was adapted for our measurements. The experiments were conducted at 60° C, the thermostatic control being effected with the help of Heppler's ultrathermostat.

Figure 1 shows stress relaxation curves for the unfilled vulcanizates of SKS-30A with varying amounts of sulfur and times of vulcanization. It is apparent that by plotting time on a logarithmic scale, the law of stress relaxation turns out to be linear. A linear drop persisted for eight hours without the appearance of any kind of deviation—an indication of the lack of any approach to a state of equilibrium. This result prevented us from measuring an "equilibrium" modulus. It is apparent from Figure 1 that at constant stress, the slope of the straight lines remains identical for all the SKS-30A vulcanizates. This regularity shows that the vulcanizates have a characteristic stress at a fixed moment of time (in our experiments—one hour). By comparing the stress to the strain, one can determine the modulus of elasticity. This value, designated by us as the pseudoequilibrium modulus (E_{yp}), was adopted for measuring the crosslink density.

* Translated from *Zhur. Tekh. Fiz.* **27**, 702-06 (1957).

TABLE [a] I

Starting rubber	Accelerator	$\frac{100\,\partial\sigma}{\epsilon\,\partial t}$
Smoked sheets	MBT	0.20
SKI	MBTS	0.25
SKB	DPG	0.35
SKN-26	MBT	0.60
SKS-30A	DPG	0.80

[a] ϵ—relative elongation; σ—stress, kg/cm²; t—time in min.

It should be noted that the slope of the stress relaxation curves of this rubber is distinguished from that for other types (see Table I). Hence one can judge the crosslink density by the magnitude of the pseudoequilibrium modulus only for similar types of rubber.

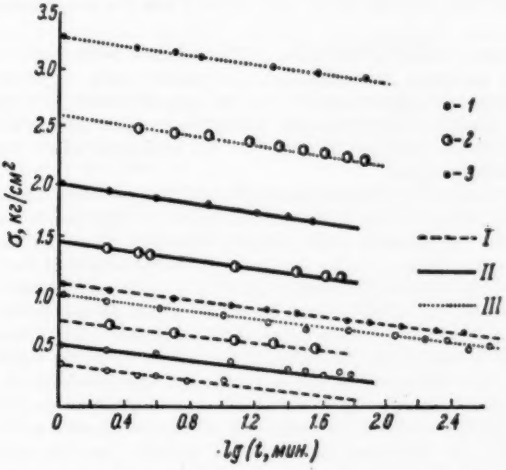


FIG. 1.—The stress relaxation of the unfilled SKS-30A vulcanizates, DPG accelerated; temperature of vulcanization 143°. Ordinate σ, kg/cm²; abscissa, ln t, min. *1*—1 part sulfur; *2*—2 parts sulfur; *3*—4 parts sulfur. *I*, *II*, *III*—20, 60, 120 minutes of cure.

In Figure 2 is shown the dependence of the rebound elasticity upon the temperature for the SKI vulcanizates. From Figure 2 it is apparent that as the pseudoequilibrium modulus increases, not only does the rebound increase, but its temperature coefficient is also changed. For vulcanizates with low crosslink densities, the rebound drops with increase in temperature. With increase in crosslink density, the temperature coefficient of the rebound, negative for low crosslink densities, gradually decreases in magnitude, eventually levels off and then begins to increase, with increasing crosslink densities. A similar regularity is observed for all the rubbers studied.

In Figure 3 is shown the dependence of the dynamic modulus of elasticity on temperature for the SKS-30A vulcanizates with various crosslink densities. One can see that with an increase of the pseudoequilibrium modulus of elastic-

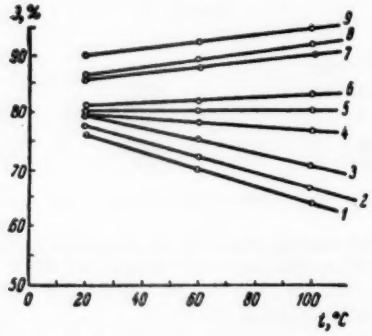


FIG. 2.—The dependence of the rebound elasticity (ordinate) on the temperature; SKI vulcanizates. Curves *1–9*: E_{pp} =1.8, 4.7, 7.9, 12.4, 12.5, 14.9, 22.2, 23.0, 27.0, kg/cm², respectively.

ity, the dynamic modulus increases. The negative temperature coefficient of the dynamic modulus is diminished in absolute value in proportion to the increase in lattice crosslink density. In the case of the larger values of pseudo-equilibrium modulus, the dynamic modulus remains practically unchanged ever a temperature range of 20–100° C. An analogous effect was observed in the case of other rubbers.

A comparison of the rebound elasticity with the pseudoequilibrium modulus for the SKS-30A vulcanizates is given in Figure 4. The points on these curves correspond to vulcanizates with varying amounts of sulfur, accelerator, or temperatures and times of vulcanization. It is apparent that there is a correlation between the rebound elasticity and the pseudoequilibrium modulus: the curves at 20°, 60°, and 100° C intersect just about at one point. Analogous curves are obtained for the other types of vulcanizates. The rebound elasticity increases with temperature for vulcanizates which lie to the right of the intersection; for those lying to the left of this point, the elasticity diminishes with increase in temperature. Hence the rebound elasticity correlates with the pseudoequilibrium modulus, independent of the compound and conditions of vulcanization. By changing the crosslink density, one can obtain with the same rubber a predetermined rebound elasticity and temperature dependence (over the indicated temperature range).

In Figure 5 a comparison is given of the dependence of the rebound elastic-

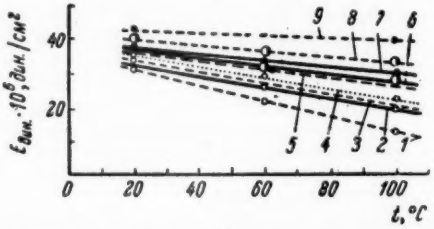


FIG. 3.—The dependence of the dynamic modulus $E_{dyn} \cdot 10^6$ dyn/cm² (ordinate) on the temperature *t*, ° C; SKS-30A vulcanizates. Curves *1–9*: E_{pp} =0.5, 2.4, 4.7, 6.8, 7.7, 11.7, 16.7, 22.9, 30.2 kg/cm², respectively.

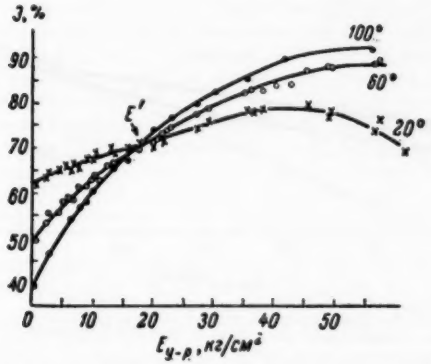


FIG. 4.—The dependence of rebound elasticity (ordinate) on pseudoequilibrium modulus for SKS-30A vulcanizates. E_{yp} (the abscissa) was measured at 60° C.

ity at 100° C on the pseudoequilibrium modulus for vulcanizates from various types of rubber. For each of the rubbers represented, the elastic rebound turns out to be uniquely related to the pseudoequilibrium modulus, independent of the changes in the percentages of vulcanizing agents and the conditions of vulcanization. The curves show that the nature of the rubber exerts considerable influence upon this dependence. We feel that a study of the effect of the base rubber on the properties of the vulcanizates may be practical only by an analysis of similar regularities.

Figure 6 illustrates the dependence of the dynamic modulus on the pseudoequilibrium modulus and definitely shows a connection between these values (the greater scattering of the points is due to a larger error in the determination of the dynamic modulus). One can see from Figure 6 that the dynamic modulus increases with increase in the pseudoequilibrium modulus. At a certain point (the smaller, the higher the temperature) the difference between these values practically disappears. The dotted line indicates the coincidence of both moduli. It is noted that with the decrease of the pseudoequilibrium

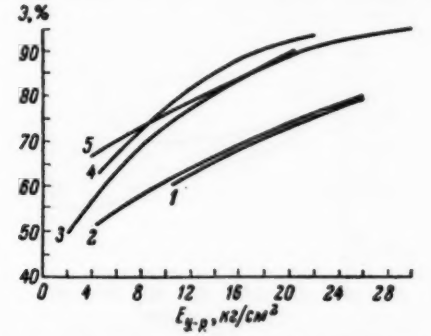


FIG. 5.—The dependence of rebound elasticity (100° C) on the pseudoequilibrium modulus for SKS-30A vulcanizates.

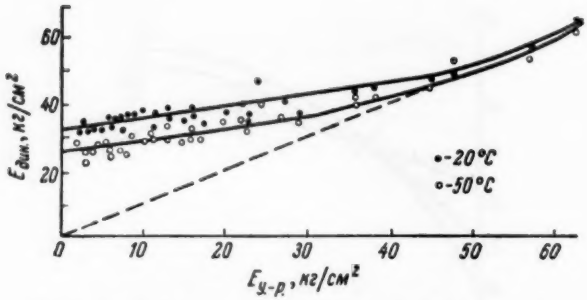


FIG. 6.—The dependence of the dynamic modulus (ordinate), $E_{дин}$ on the pseudoequilibrium modulus for SKS-30A vulcanizates.

modulus to zero (raw rubber), a value for the dynamic modulus still persists. Analogous results are also observed with the other types of rubber.

Figure 7 illustrates the dependence of the internal-friction modulus K_E (specific mechanical loss, based on the square of deformation[7]) on the pseudo-equilibrium modulus for the vulcanizates prepared from SKS-30A. At 60° C, the friction modulus drops as E_{yp} increases; at higher values of the latter, the friction modulus passes through a minimum, even though the readings were not highly precise. A distinct minimum is observed at E_{yp} = 40 kg/cm² for the curve at 20°.

The peculiarities of the temperature dependence of the dynamic characteristics upon the degree of vulcanization may be explained in the following manner.

The chain molecules of the vulcanizate are joined in a network both by strong chemical bonds and by weaker physical bonds, the number and strength of which abruptly decreases with increase in temperature. On the one hand, with increase in temperature, the rebound elasticity rises because of the increasing mobility of the chains (the relaxation time of the segmental movements of the molecules diminishes) in the vulcanizate network. On the other hand, the increase of temperature leads to a weakening of the physical bonds and a decrease in their number, involving a drop in the number of chain sections

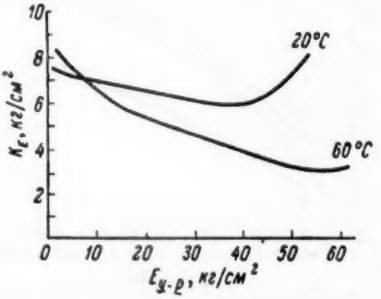


FIG. 7.—Dependence of the internal-friction modulus K_E on the pseudoequilibrium modulus of the SKS-30A vulcanizates.

bound in the spatial network and imparting elasticity to it; correspondingly, the number of chains which have no connection with the network or remain "bound" to it only at one end is increased. The latter result hinders the movement of the resilient elements of the rubber structure and lowers the elasticity. In rubber for which $E_{yp} < E'$ (see Figure 4), it seems that this latter condition prevails and as a consequence, the elasticity is reduced with increasing temperature. In the area where E' and E_{yp} are about the same, both factors compensate so that the elasticity does not change with change in temperature. Finally, for the case where $E_{yp} > E'$, an increase of chain mobility predominates, whereupon the elasticity increases with increase in temperature.

With these facts in mind, it is possible to explain also the effect of temperature on the dynamic modulus. At lower temperatures, the physical bonds play a greater role, hence the dynamic moduli of the weakly and strongly vulcanized rubbers at 20° C do not differ too greatly. At high temperatures this difference is more manifest owing to the fact that the physical bonds weaken with increase in temperature and the chemical bonds become relatively more effective. If one compares the dynamic modulus with the pseudoequilibrium modulus during vulcanization, then it is apparent that as E_{yp} increases by more than a factor of 10, E_{dyn} increases by only a factor of 3.

This is due to the fact that the pseudoequilibrium modulus on the whole reflects the presence of the chemical bonds and hence is sensitive to the degree of vulcanization. The dynamic modulus principally reflects the presence of physical bonds.

Thus the properties of unfilled vulcanizates from the same rubber base are uniquely determined by the crosslink density. By controlling the pseudoequilibrium modulus, it is possible to obtain rubbers with various predetermined characteristics by varying the recipes and the conditions of vulcanization (variation in the percentages of vulcanization agents and the time and temperature of vulcanization).

The dependence of dynamic elastic properties on the degree of vulcanization is advantageous for the preparation of vulcanizates from various base rubbers. A comparison of these relations may serve as a method for showing the effect of the nature of the raw rubber on the properties of the vulcanizate.

The method of measuring the pseudoequilibrium modulus is not difficult: the whole experiment takes twenty minutes. Hence, characterization of a vulcanizate by the pseudoequilibrium modulus seems to us to be a highly expedient and commendable method.

REFERENCES

[1] Bartenev, G. M., *Zhur. Tekh. Fiz.* **22**, 1154 (1952).
[2] Flory, P., *Ind. Eng. Chem.* **38**, 417 (1946).
[3] Flory, P., Rabjohn, N., and Shaffer, M., *J. Polymer Sci.* **3**, 435 (1949).
[4] Dogadkin, B. A., and Heifetz, F., *Kolloid. Zhur.* **14**, 157 (1952).
[5] Adams, H., and Johnson, B., *Ind. Eng. Chem.* **45**, 1539 (1953).
[6] Reznikovskii, Yurovskaya, V. S., and Dogadkin, B. A., *Kolloid Zhur.* **14** (1952).
[7] Kuvshinskii, E. V., and Sidorovich, E. A., *Zhur. Tekh. Fiz.* **26**, 878 (1955).

INTERMOLECULAR INTERACTION IN RUBBER SOLUTIONS*

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As has already been shown, the nature of the intermolecular interaction is one of the basic factors determining a number of properties of rubbers and vulcanizates[1]. The effects of intermolecular action on molecular light scattering in solutions of nitrile rubbers have also been studied[2]. In the present investigation, the influence of intermolecular interaction on the properties of polymer solutions has been studied by viscosity and swelling determinations.

In order to study the influence of intermolecular interaction on the properties of polymers and their solutions, it is necessary to have a series of polymers which differ in the degree of intermolecular interaction but with all the other structural characteristics constant. For example, if the light scattering method is used, the chain length and branching should be the same for all the polymers. If the swelling method is used, the degree of crosslinking should be the same in all the polymers. Finally, for viscosity determinations the polymers should also have the same molecular weight and degree of branching.

Four types of intermolecular interaction in polymer solutions are usually considered: 1) between regions of the same polymer chains; 2) between individual polymer molecules; 3) between molecules of the polymer and solvent; 4) between the solvent molecules.

The first and third of these types of interaction have the predominant influence on the viscous properties and molecular light scattering of rubber solutions, while in swelling the principal role is played by the second type of interaction. Thus, studies of the properties of polymers by light scattering, viscometry, and swelling provide a complete picture of the influence of intermolecular interaction on the properties of polymers and their solutions. Interaction between the solvent molecules does not seem to be significant in investigations like ours, although there are indications[3] that it must be taken into account in some cases.

Guided by the foregoing considerations, we chose standard butadiene-acrylonitrile copolymers (SKN-18, SKN-26, and SKN-40), containing different proportions of acrylonitrile, as the materials, and these were studied by viscosity and swelling methods.

The polymers were purified and fractionated for the viscosity determinations. The purification was effected by double reprecipitation by dehydrated methyl alcohol from solutions in benzene, in an atmosphere of pure nitrogen. The fractionation consisted of fractional precipitation of the polymers from benzene solutions with cooling to 0°. The fractions were dried in nitrogen and dissolved in methyl ethyl ketone. These solutions were used for determinations of the molecular weights of the fractions and for the viscosity measurements. The molecular weights of the fractions were determined by the light scattering

* Reprinted from *Colloid Journal* 19, 553–556 (1951): an English translation by Consultants Bureau, Inc. of *Kolloidnyĭ Zhurnal* 19, 553–556 (1957).

TABLE I

MOLECULAR WEIGHTS OF DIFFERENT FRACTIONS OF NITRILE RUBBERS

Rubber	Molecular weights of fractions			
	I	II	III	IV
SKN-18	148,000	57,100	19,250	—
SKN-26	—	312,000	87,800	48,200
SKN-40	148,000	100,000	46,700	28,400

method previously described[2]. The results of these determinations are given in Table I.

For studying intermolecular interaction by the swelling method, the polymers were converted into unfilled vulcanizates of the following composition (in parts by weight):

Rubber	100
Sulfur	2
Sulfenamide BT	1.8
Zinc oxide	5
Stearic acid	2
PBNA	1

The density ρ by the double weighing method, and the equilibrium elasticity modulus E_∞ by a dynamometer of the Polanyi type, were determined for these vulcanizates, and the molecular weights of the chains M_c were then calculated by means of the equation[4]:

$$M_c = N_a \cdot 3k \cdot T\rho / E_\infty \tag{1}$$

where N_a is the Avogadro number; k is the Boltzmann constant; T is the absolute temperature.

The greatest deviation between the values of M_c was only 6%. Therefore the degree of crosslinking was practically the same in all three vulcanizates; this satisfies the above condition for the applicability of the swelling method.

The viscosity determinations were carried out with three efflux velocity gradients in a special capillary viscometer[5], the measuring portion of which consisted of three bulbs arranged vertically. The efflux velocity gradient dv/dx is calculated by means of the equation

$$\frac{\partial v}{\partial x} = \frac{A}{\eta/d} \tag{2}$$

where A is a constant found by calculation; η/d is the kinematic viscosity, determined from the equation

$$\eta/d = \alpha(t - \beta/dt) \tag{3}$$

where α and β are constants for the apparatus; t is the efflux time.

The constants α and β were found by determinations of the viscosity of water; the efflux time was measured by a seconds clock to an accuracy of 0.2 second. The efflux times were used to calculate the specific viscosity η_{sp}, the reduced viscosity η_{sp}/c, and the velocity gradient. The following relationships

were plotted for each bulb of the viscometer, situated at a definite height:

1) η_{sp}/c against the concentration c. Extrapolation to $c \rightarrow 0$ gave the intrinsic viscosity $[\eta]$;

2) logarithm of the efflux velocity gradient against the concentration. This was also extrapolated to $c \rightarrow 0$ to determine the efflux velocity gradient at zero concentration $[dv/dx]$.

The values found for $[\eta]$ and $[dv/dx]$ were used to plot the logarithm of the intrinsic viscosity against the velocity gradient. Extrapolation of this graph to zero velocity gradient gave values for the viscosity at zero concentration and zero efflux velocity gradient, i.e., values which were entirely independent of the experimental conditions.

Figure 1 shows log $[\eta]$ plotted against $[dv/dx]$ for fractions of different

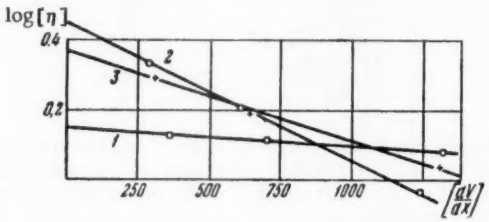


FIG. 1.—Variation of intrinsic viscosity with limiting velocity gradient for fractions of similar molecular weight: *1*) SKN-18 (M-57,000); *2*) SKN-26 (M-48,200); *3*) SKN-40 (M-46,700).

nitrile rubbers of approximately the same molecular weight (Table I). The relationships are linear, and conform to the equation:

$$\lg [\eta] = \lg [\eta]' - B[\partial v/\partial x] \tag{4}$$

where log $[\eta]'$ corresponds to the intrinsic viscosity at zero velocity gradient and zero concentration. The coefficient B differs from the different polymers used, and depends on the acrylonitrile content, i.e., on the intermolecular interaction, Table II, characterized by the square root of the cohesive energy

TABLE II

VARIATION OF SLOPE FACTORS OF VISCOSITY AND LIGHT SCATTERING CURVES AND EQUILIBRIUM SWELLING WITH DEGREE OF INTERMOLECULAR INTERACTION

Polymer	$B \cdot 10^3$	Q in %	$B_T \cdot 10^3$	$\sqrt{\frac{E}{V}}$
SKN-18	1.12	210	0.67	8.86
SKN-26	4.89	215	3.86	9.22
SKN-40	3.24	207	1.94	9.52

density[6]. The values of the slope factor B in Equation 4, the equilibrium swelling Q, the slope factors of the molecular light scattering curves, taken from an earlier paper[2], and the cohesive energy densities ($\sqrt{E/V}$) for the rubbers studied are given in Table II. The data in Table II show that the factor B does not vary steadily with $\sqrt{E/V}$. The probable reason is that changes of polymer

polarity are accompanied by changes in the difference between the nature of intermolecular interaction in the solvent and in the polymer. The less this difference is, the stronger will be the polymer-solvent interaction. With increase of this interaction the polymer molecules become more flexible, the dependence of log $[\eta]$ on $[dv/dx]$ becomes more pronounced, and the absolute value of B in Equation 4 increases. If the polarity of the polymer is increased further, the nature of the interaction between the polymer molecules will change so much that it will again differ from the nature of the interaction between the solvent molecules. This will diminish polymer-solvent interaction and therefore decrease the absolute value of B, as the polymer molecules will become more rigid and will be deformed less by flow of the solution.

To estimate the energy of intermolecular interaction, the equilibrium swelling was found by extrapolation of the plot of the degree of swelling Q against time t to $t \to 0$. Several solvents with increasing values of cohesive energy density were chosen for these experiments: ethyl ether, *n*-amyl acetate, *n*-propyl acetate, butyraldehyde, ethyl acetate, methyl ethyl ketone, ethyl formate, methyl acetate, acetone, and acetonitrile. The values of the cohesive energy

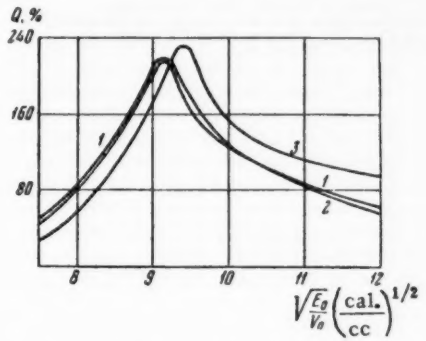


FIG. 2.—Variation of degree of swelling of nitrile rubbers with cohesive energy density of the solvent: *1*) SKN-18; *2*) SKN-26; *3*) SKN-40.

density for the polymers studied were at about the middle of this series. The values for the cohesive energy densities of the solvents were taken from Gee's paper[6].

These values were used to plot the equilibrium swelling of the three polymers against the cohesive energy densities of the solvents, as shown in Figure 2. These smoothed curves were used for determining the degree of swelling of nitrile rubbers in solvents with known values of $\sqrt{E_0/V_0}$. The results show that the maximum is displaced toward lower values of Q and $\sqrt{E_0/V_0}$ with decreasing $\sqrt{E/V}$ for the polymer.

It follows from the data in Table II that such properties as viscosity, swelling, and molecular light scattering of divinyl-acrylonitrile polymers in methyl ethyl ketone do not vary smoothly with intermolecular interaction, and vary with the polarity of the rubber, passing through a maximum.

SUMMARY

A study has been made of the viscosities of butadiene acrylonitrile rubber solutions and of the equilibrium swelling of vulcanizates of these rubbers with the same degree of crosslinking, in various solvents.

It was found that the viscosity and light scattering characteristics of the solutions, and swelling of the vulcanizates of butadiene acrylonitrile rubbers are not steady functions of the degree of intermolecular interaction, represented by the difference of the square roots of the cohesive energy densities of the polymer and the solvent but pass through a maximum with variations in the polarity of the rubber.

ACKNOWLEDGMENT

The swelling data were obtained jointly with L. A. Oksentyevich.

REFERENCES

[1] Dogadkin, B. A., and Gul, V. E., *Proc. Acad. Sci.* USSR **70**, 1017 (1950); Gul, V. E., *Colloid J.* **13**, 99 (1951); Gul, V. E., Dorokhina, T. V., and Dogadkin, B. A., *Colloid J.* **13**, 339 (1951); Gul, V. E., Sidneva, N. Ya., and Dogadkin, B. A., *Colloid J.* **13**, 422 (1951).

[2] Gul, V. E., and Klitenik, G. S., *Colloid J.* **16**, 37 (1954).

[3] Kirkwood, J. G., and Goldberg, R. J., *Chem. Phys.* **18**, 54 (1950).

[4] Bartenev, G. M., and Vishnitskaya, L. A., *J. Tech. Phys.* **20**, 858 (1950).

[5] Krigbaum, W. R., and Flory, P., *J. Polymer Sci.* **11**, 37 (1953).

[6] Gee, G., *Trans. Inst. Rubber Ind.* **18**, 266 (1943).

THE PLASTIC FLOW AND ELASTICITY OF RAW RUBBER AND RAW RUBBER MIXES *

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As is known, the deformation of raw rubber and raw rubber mixes under the action of external forces develops in two different forms, (disregarding elastic (Hookian) deformation, which is very small) because of the ability of polymeric substances to undergo reversible, elastomeric deformation, and irreversible deformation or true flow. The mechanical properties of such substances are therefore determined by their capacity to undergo both types of deformation, and should be studied in such a way as to take into account the simultaneous manifestation of both.

Detailed studies of the subject[1–3] have been carried out relatively recently, and relate only to pure undiluted rubbers. If the laws governing the development of the individual components of the total deformation of raw rubber mixes could be established, this would provide insight into the dependence of the mechanical properties both on the molecular structure of the rubber, and on the nature of the ingredients introduced into the mix. This insight, in its turn, is necessary for the development of the physical principles governing the composition of rubber mixes with required technological properties, and for the selection of rational methods for the laboratory testing of raw mixes.

The present communication contains certain data obtained in an investigation of the properties of raw mixes with the object of determining the laws which govern the development of the different components of the total deformation.

METHOD OF INVESTIGATION AND INTERPRETATION OF RESULTS

The mechanical properties of rubbers and mixes were studied by the method of uniaxial compression of cylindrical specimens, 10 × 10 mm.

The rubbers, and also the milled mixes, contained considerable porosity, which could distort the results of the determinations. To remove the pores, the materials were rolled to give the thinnest possible films, which were stacked into sheets of the required thickness. Each sheet was placed in the middle of a cylindrical mold, where it was slowly pressed under a hydraulic press until excess of the mixture flowed out through the gap between the plunger and the mold. After 2–3 days under pressure, the sheet was removed from the mold and then stored for several days at room temperature to allow the stresses to decay. To complete the relaxation, the sheet was placed for 3 hours in a thermostat at 55–60°. Specimens cut from the sheets were subjected to additional relaxation at room temperature for several days.

The specimens were assumed to be at equilibrium when their height became constant as measured by means of a micrometer with 0.01 mm divisions. It

* Reprinted from *Colloid Journal* **20**, 137–141 (1958); a translation by Consultants Bureau, Inc. of *Kolloidnyĭ Zhurnal* **20**, 143–148 (1958).

must be pointed out that this cannot be regarded as a strict enough criterion; it merely indicates that the stresses which arose during preparation of the specimens had relaxed to the extent which is possible at room temperature. For true equilibrium the specimens must be kept for a long time at elevated temperatures, which gives rise to pore formation. Moreover, experiments showed that exposure to high temperatures apparently causes chemical changes in the raw mixes, so that consistent results cannot be obtained in measurements of the mechanical properties. As the specimens were not quite in equilibrium, this introduced some degree of uncertainty into the quantitative studies. However, we considered that it was preferable to study specimens containing certain internal stresses rather than specimens of changed chemical composition.

A Hüppler consistometer, modified for our purposes, was used for the determinations. The specimens were placed in a cylinder 20 mm in diameter, contained in a thermostat, and were compressed by means of a piston to which a load was applied through a rod. To diminish end effects, the ends of the specimens were smeared with glycerol. After the specimens had been held for 15 minutes at the temperature of the experiment, they were compressed at constant load. The displacement of the piston during compression was recorded as a function of time. At the end of the predetermined time, the specimen was removed and restored by immersion in boiling water for 30 minutes. The experiments were performed at 40, 70, 100, and 120°. The mechanical properties at a given load were calculated from the following data: initial height of the specimen H_1, height under load after a definite time H_2, and height after restoration of the deformed specimen at 100° followed by 24 hours at room temperature, H_3; H_1 and H_3 were measured by means of a micrometer at room temperature, and H_2 was read off on the consistometer scale at the temperature of the experiment. The deformability was assessed as the true deformation, defined as the integral, between the initial and final lengths, of the ratio of an infinitesimal length change at a given instant to the actual length H at the same instant:

$$D = \int_{H_1}^{H_2} \frac{dH}{H} = \ln \frac{H_2}{H_1}$$

In accordance with the accepted designations, we have the following expressions for the total (D), plastic (D_p) and high-elastic deformation.

$$D = \ln \frac{H_2}{H_1}; \quad D_p = \ln \frac{H_3}{H_1}; \quad D_{he} = \ln \frac{H_2}{H_3}$$

It is seen that

$$D = D_p + D_{he}$$

As the true stress varied during deformation, the "coefficient of viscosity" was calculated as the ratio of the integral $\int_0^\tau \sigma(\tau)d\tau$ to the value of the plastic deformation which developed during the whole time of action of the load τ. The integration was performed graphically by measurement of the area of the experimentally found curve for the variation of the total relative deformation

with the time τ,

$$\int_0^\tau \sigma(\tau)d\tau = \int_0^\tau A(1-\epsilon)d\tau = \int_0^\tau A\lambda(\tau)d\tau = A\int_0^\tau \lambda(\tau)d\tau$$

where the stress $\sigma(\tau)$ at the given instant, the total relative deformation $\epsilon(\tau)$ at the same instant, and the stress A calculated for the initial cross section are connected by the expression $\sigma = A(1-\epsilon)$ or $\sigma = A\lambda$, which is valid if the volume remains unchanged during the deformation; λ is the relative length of the specimen.

Thus, the viscosity was calculated by means of the formula

$$\eta = \frac{\int_0^\tau \sigma(\tau)d\tau}{D_p} = \frac{A\int_0^\tau \lambda(\tau)d\tau}{D_p}$$

It may be noted that if $\eta = \text{const}$, from $\eta = \dfrac{\int_0^\tau \sigma d\tau}{D_p}$ we have $\sigma = \eta\dfrac{dD_p}{dt}$, which is Newton's generalized viscosity equation. This was the reason for our choice of η for characterization of the plastic properties. To characterize the high-elastic properties, we determined the elasticity modulus, defined as the ratio of the stress acting on the specimen before removal of the load to the true high-elastic deformation

$$E_{he} = \frac{A\lambda}{D_{he}}$$

The initial stress was varied from 0.13 to $1.86\cdot10^6$ dynes/cm^2, and the deformation time, from 3 to 300 minutes. Rubber mixes based on SKB-50_{sv} were used in the study. The mixes did not contain vulcanizing ingredients. The mixes contained, in parts by weight, 100 rubber, 5 each of Rubberax, asphalt, and zinc oxide, 2 of oleic acid, and 45 carbon black (channel black in Mix 1 and lamp black in Mix 2). Experiments were also performed on rubbers without added ingredients and on three-component mixtures containing 100 parts of rubber, 2.5 of stearic acid, and 45 of carbon black (channel black in Mix 3 and lamp black in Mix 4). The deformation conditions for the rubbers and three-component mixtures are given in the account of the experimental results. The results of the determinations are given in CGS units.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 gives the curves for the development of total deformation and the individual components of the deformation in SKB-50_{sv} rubber and mixes containing channel black (Mix 3) and lamp black (Mix 4). It would have been desirable to compare the behavior of these systems under the same compression conditions; however, owing to the sharp change of properties produced by introduction of carbon black this condition could be only partially satisfied with the experimental procedure used. The greatest deviations from uniform deformation, which could distort the results, were found in the original rubber.

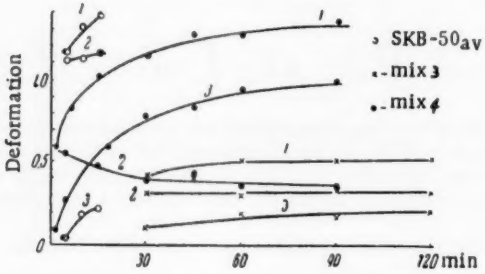


FIG. 1.—Development of deformation of SKB-50_{av} rubber and of Mixes 3 and 4; $t = 70°$; $A = 0.62 \cdot 10^6$ dynes/cm²: *1*) total deformation; *2*) high-elastic component; *3*) plastic component.

It follows from Figure 1 that the pure rubber is deformed more easily than its mixtures, and this is due to high-elastic deformation, as the plastic component of the deformation is small. Introduction of carbon black decreases the total deformation. The two blacks differ little in their effect on the reversible high-elastic deformability, the absolute values of the high-elastic deformation of Mixes 3 and 4 being similar. The nature of the black mainly influences the plastic deformation. As a result, the deformation components are in a different ratio in the two mixes. Under the same experimental conditions, mixes containing channel black are characterized by a higher ratio of the high-elastic to plastic component in the total deformation, as compared with mixes containing lamp black. Accordingly, the coefficient of viscosity and elasticity modulus are higher in mixes with channel black than in mixes with lamp black (Figure 2). Thus, although the two blacks decrease the high-elastic component of the deformation to approximately the same extent, they confer different viscoelastic properties on the mixes.

The variations of the viscoelastic characteristics of Mix 2 with the time of deformation and the load at different temperatures are given in Figures 3 and 4; similar relationships hold for Mix 1.

It follows from these results that the elasticity modulus can either decrease or increase with time. The direction of the change of the elasticity modulus

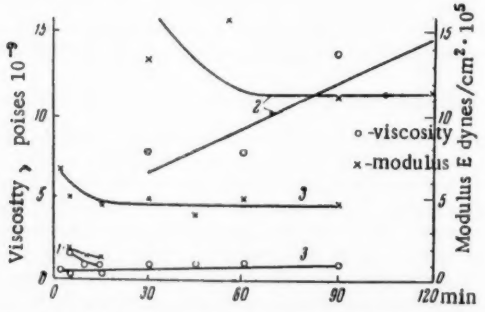


FIG. 2.—Effect of the time of deformation on the viscosity and modulus of elasticity of SKB-50_{av} rubber and Mixes 3 and 4; $t = 70°$; $A = 0.62 \cdot 10^6$ dynes/cm²: *1*) SKB-50_{av}; *2*) Mix 3; *3*) Mix 4.

depends on a number of factors. At temperatures below 70° the elasticity modulus decreases with time at all the stresses used. At higher temperatures, the elasticity modulus increases with time. The greater the compressive force, the greater is this increase; it is evidently the result of chemical or physicochemical structural changes in the material under these conditions. Decrease of temperature and of the stress diminishes the role played by these changes and thereby favors relaxation processes which lead to a decrease of the elasticity modulus. These results suggest that the modulus of elasticity of raw rubber mixes as a function of the time of action of the force has a minimum. It seems that in our experiments only isolated portions of this general function were observed. Which portion of the complete curve (descending or ascending) was actually observed in a particular experiment depended on the temperature and the force. At lower temperatures, when chemical and physicochemical proc-

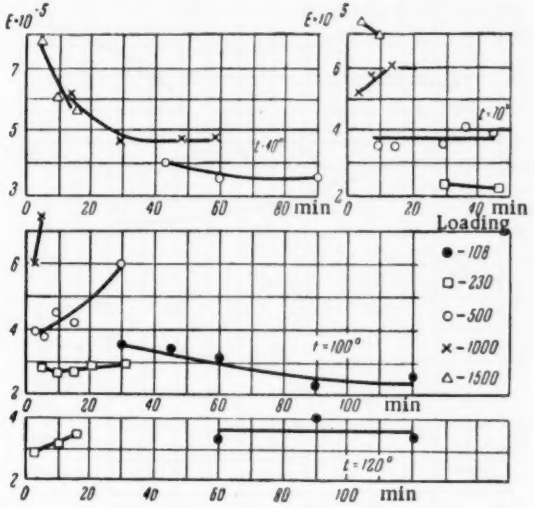


FIG. 3.—Effects of time, temperature, and stress on the modulus of high elasticity of Mix 2.

esses develop slowly, relaxation of stress with time is the predominant effect. At high temperatures these processes become appreciable, while the relaxation is so rapid that it is complete at the very start of the experiment. Therefore the modulus increases with time; the rate of increase naturally depends on the temperature and the force, which are the principal factors governing the mechanochemical processes which develop.

Examination of Figure 4 shows that the variations of viscosity with the time of action of the force, the magnitude of the force, and the temperature are also of a complex character. At 40° the viscosity decreases with time for small acting forces. At higher temperatures and at larger stresses the viscosity nearly always increases with time. It is possible that the complete viscosity-time curve also shows a minimum. Under the action of the applied force the

structure of the raw rubber mix gradually breaks down, and the viscosity therefore decreases with time. During flow, however, the chain molecules are straightened, and chemical and physicochemical processes altering the structure also develop. These changes produce a gradual increase of viscosity. Naturally, at low temperatures and small stresses the predominant process is the gradual breakdown of the structure of the raw rubber mix, and therefore the viscosity decreases with time under such conditions. Conversely, the structure breaks down rapidly at high temperatures or large stresses, and the only effect actually observed is the development of chemical and physicochemical processes leading to structurization. At low temperatures and large stresses the viscosity increase may be attributed to the development of elastic deformation.

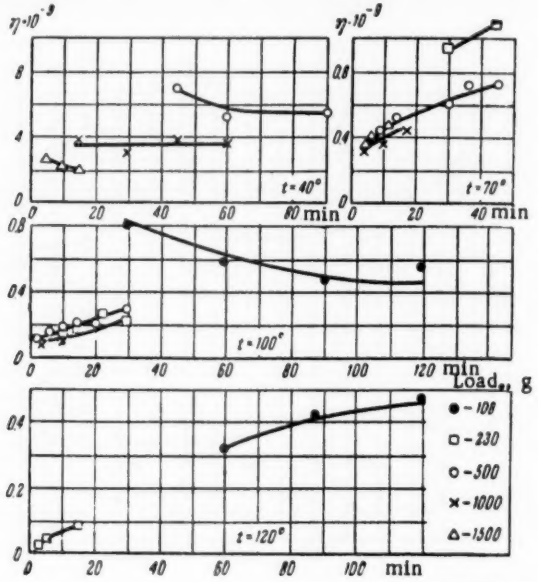


FIG. 4.—Effects of time, temperature, and stress on the coefficient of viscosity of Mix 2.

The effect of temperature on the stress-viscosity and stress-modulus relationships is very peculiar. The influence of the stress on the modulus of elasticity increases at higher temperatures, whereas the viscosity only depends on the stress at lower temperatures.

All these peculiarities of the mechanical behavior of raw loaded rubber mixes indicate that their characteristic feature is the variability of structure in the course of deformation. Little is known as yet about the mechanism of the variations of the structure of raw loaded rubber mixes during deformation, but it is quite evident that it depends on the chemical reactivity of the raw mixes and the variability of the structure formed by the rubber-carbon mixes.

SUMMARY

Data have been obtained on the mechanical properties of rubber, two-component rubber-carbon black systems, and loaded raw rubber mixes at various temperatures and under different stresses.

The true viscosity and the elasticity modulus of a raw rubber mix depend on the time, temperature, and the magnitude of the applied force; it is suggested that this is a consequence of the variability of the structure of the mix under stress and on heating.

REFERENCES

[1] Treloar, L., *Trans. Faraday Soc.* **36**, 538 (1940).
[2] Kargin, V. A., and Sogolova, T. I., *J. Phys. Chem.* **23**, 540, 551 (1949).
[3] Bartenev, G. M., *J. Phys. Chem.* **24**, 1210 (1950).

TENSILE STRENGTH OF FILLED SBR VULCANIZATES *

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INTRODUCTION

The molecular behavior responsible for the observed tensile strength properties of unfilled rubbers has been studied in a recent paper from this laboratory[1]. In the present paper we intend to extend that work to the case of rubbers which are filled with carbon black. Measurements of the tensile strength of hot and cold SBR as a function of carbon black concentration, degree of vulcanization, and temperature are reported. An attempt is made to interpret the observed behavior in terms of molecular concepts. Some additional measurements with resin and calcium carbonate fillers are shown to lend support to the conclusions reached.

EXPERIMENTAL

Tensile strength were measured in two different ways. Measurements at room temperature were made with a Dillon tester operating at a rate of elongation of five inches per minute. The samples used were of the standard dumbbell type, about $1/8 \times 1/20$ inches in cross section. At other temperatures, the measurements were made at a constant rate of loading of about 1500 psi/min. All points reported are the average of five separate tests.

The rubbers were compounded at the Goodyear Tire & Rubber Company under the direction of Dr. S. D. Gehman. Standard recipes were used. Vulcanization was carried out in a Carver press at 250° F.

The degree of crosslinking was computed from swelling measurements in benzene by use of the following relation:

$$\nu_e = -\frac{v_0}{V_s}\frac{\ln(1 - v_r) + v_r + \mu v_r^2}{v_r^{\frac{1}{3}}v_0^{\frac{1}{3}} - 1/2\, v_r} \tag{1}$$

In this equation, ν_e is the number of *effective* network chains per unit volume based on the original rubber, v_0 is the volume fraction of network rubber in the original stock, V_s is the molal volume of the solvent, and v_r is the volume fraction of rubber in the swollen stock. The Huggins solubility parameter, μ, was taken to have the value given by Krause[2], $\mu = 0.37 + 0.27v_r$. In this regard, it is important to notice that ν_e is changed an appreciable amount by stretching the rubber to its limit. Unless stated otherwise, the ν_e values given were determined on the rubber *after* it had been stretched. The reasons for this choice will be pointed out in a later section.

RESULTS

The tensile strength data for SBR 1006 and 1500 containing 30 parts of HAF black and vulcanized with either sulfur or TMTD are shown in Figures 1, 2,

* Reprinted from the *Journal of Polymer Science*, Vol. 33, Issue No. 126, pages 259–271, December 1958.

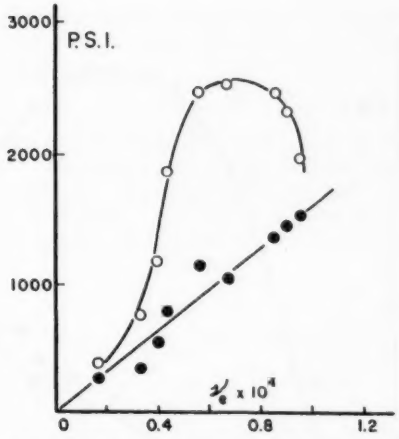


FIG. 1.—Tensile strength (○) and 300% modulus (●) for SBR 1006 containing 30 parts per hundred rubber of HAF black. ν_e is measured in moles per cc.

and 3. Data for the 300% modulus are also given in these figures. In Figure 4, data for SBR 1006 containing 50 parts of black are shown. For this particular case, we have plotted the data in two ways, against ν_e determined for the stretched and also for the unstretched rubbers. Figure 5 shows similar

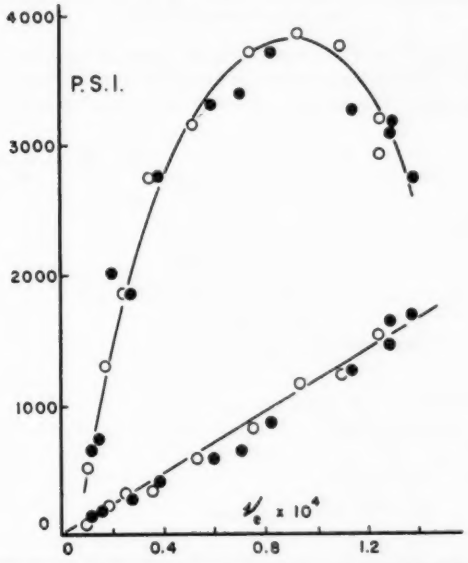


FIG. 2.—Tensile strength and 300% modulus for SBR 1500 containing 30 parts HAF black. The vulcanizing agent was three (○) and four (●) parts TMTD.

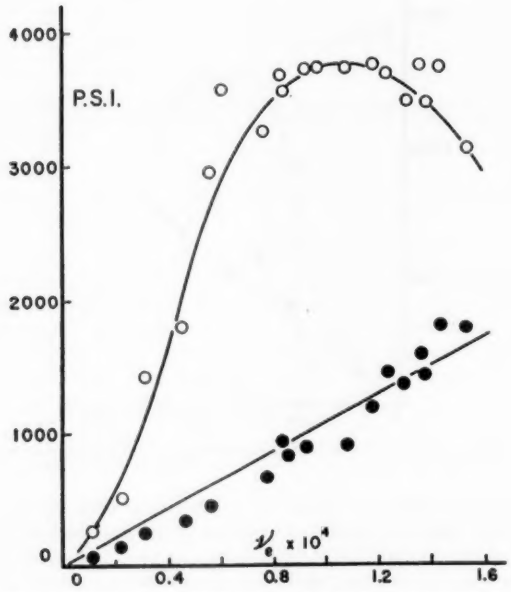


FIG. 3.—Tensile strength (○) and 300% modulus (●) for SBR 1500 containing 30 parts black and vulcanized with sulfur.

data for both SBR types when filled with 45 parts of calcium carbonate (Calcene TM). The effect of temperature is also shown in this figure. In addition, the comparison curve for the gum stock is given. Figure 6 shows how the

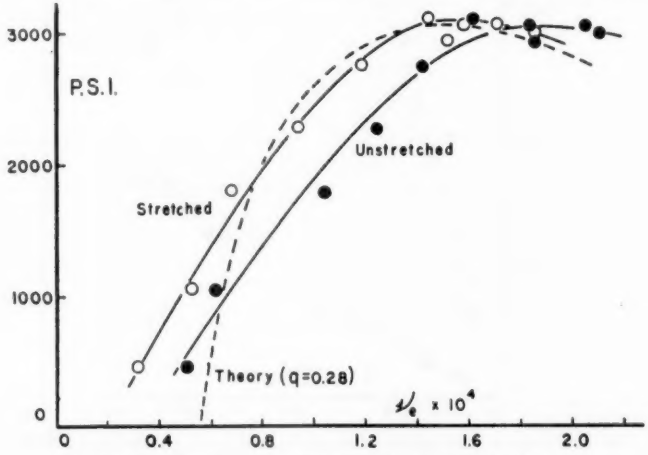


FIG. 4.—Tensile strength of SBR 1600 containing 50 parts black.

tensile strength of carbon black reinforced stocks depends on temperature. Figure 7 shows similar data for SBR 1500 filled with a high styrene-butadiene filler (Pliolite S-6).

THEORY

The above results can be explained qualitatively on the basis of a theory recently presented[1]. This theory shows that, in a rubber under stress, a few of the chains are much more highly strained than is the average chain. It is these chains which break first. However, the sample will break only if the rupture of one chain leads, on the average, to the rupture of one or more neighboring chains.

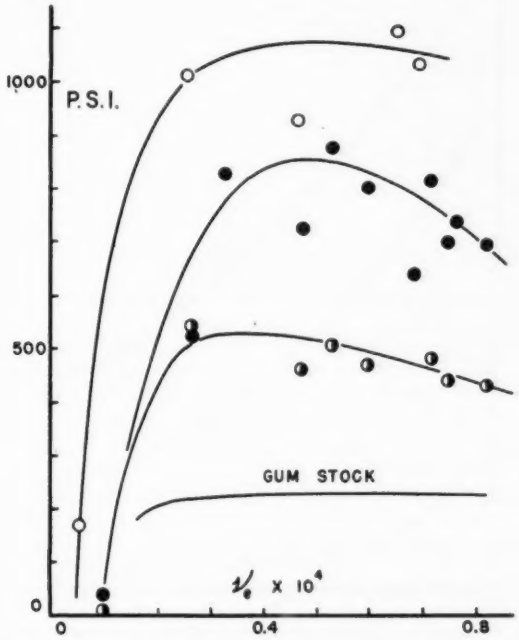


FIG. 5.—Tensile strength of SBR containing 45 parts calcium carbonate: (○) SBR 1500 at 23° C; (●) SBR 1006 at 23° C; and (◑) 70° C.

The theory assumes that, in the case of unfilled noncrystallizable rubbers, each chain which breaks transfers its load to two neighboring chains. If, on the average, one neighbor chain breaks under the extra load, then the break will propagate, and the sample will fail. The theory leads to the following equation for tensile strength (T.S.):

$$\text{T.S.} = (\nu_e/3)^{\frac{1}{2}}\, \mathfrak{F}_c\, [1/(1 + 0.61x) - q] \qquad (2)$$

where

$$x = 2(a\mathfrak{F}_c/KT\sigma)^{\frac{1}{2}}$$

In this equation, ν_e is the effective number of network chains in unit volume, $\mathfrak{F}_c$ is the force which will break the weakest chain link, σ is the average number of possible crosslink sites between actual crosslinks and a is the length of a chain segment. The quantity q, which is equal to 1/2 for gum stocks, is equal to the fraction of the extra load shared by each neighbor of a broken chain.

To a first approximation at least, the effect of fillers and crystallization is to increase the number of chains which share the load of a broken chain. One of many possible ways in which this can be accomplished is shown schematically in Figure 8. When chain AB breaks at X, it is clear that less than half the load

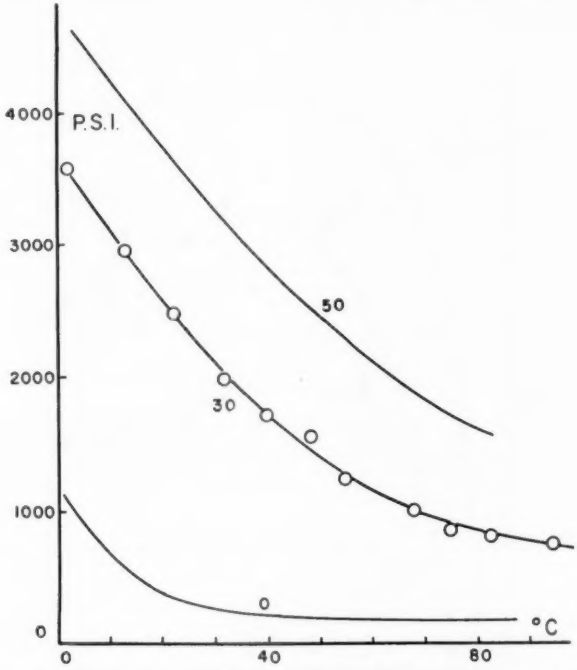


FIG. 6.—Temperature variation of strength for SBR 1006 containing the indicated quantities of HAF black.

held by this chain will be transferred to chain CD. Part of the load is held by the crystals or filler particles which, in turn, distribute it over a large number of chains. This necessitates that q in Equation (1) be replaced by a smaller number. If the filler does not interact with the rubber, q will be 0.50. Any increase in filler-rubber bonds, whether by changing the nature of the filler surface, increasing the surface area of filler, or lowering the temperature, should result in a decrease in q.

The effect of primary molecular weight of the rubber is also illustrated by Equation (1). It is clear that the rubber cannot show appreciable strength under slow tests unless a gel structure exists in the rubber. This is the basis

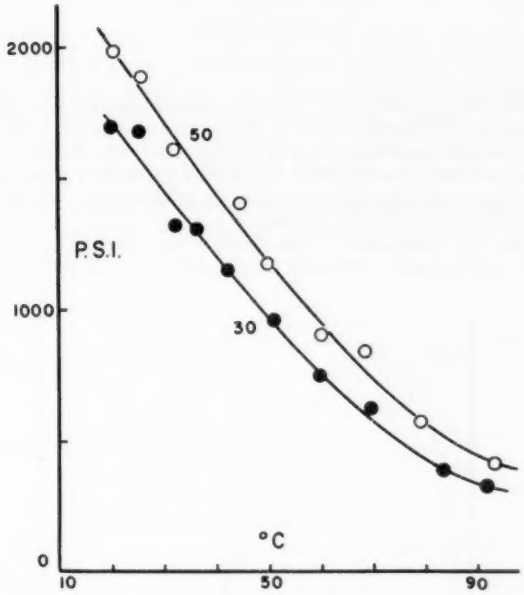


FIG. 7.—Tensile strength of SBR 1500 containing the indicated quantities of Pliolite S-6.

for the appearance of the factor $(\nu_e)^{\frac{1}{2}}$ in Equation (1). To a first approximation, one can identify the quantity ν_e with the effective number of network chains found from the swelling measurements. Using Flory's notation[3], one has

$$\nu_e = \nu(1 - 2M_c/M_n) \tag{3}$$

where ν is the number of crosslinked chain units. Actually, as shown in Figures 1–5, the strength decreases to zero when ν_e is of the order of 0.10×10^{-4} mole/cc. This is probably the result of the fact that some of the network chains are unable to assist in supporting the load because they are not suffiicently well anchored to surrounding chains. For the purposes of comparing theory and experiment, we shall correct the swelling values of ν_e by subtracting the small discrepancy indicated.

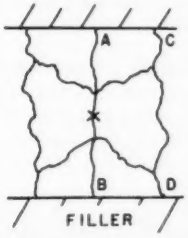


FIG. 8.—A schematic diagram to show filler action.

DISCUSSION

GUM STOCKS

It has been shown previously[1] that the data of Taylor and Darin for the tensile strength of SBR gum stock[4] can be described reasonably well by Equation 2. Surprisingly, unlike the data of Taylor and Darin, data obtained in this laboratory on ordinary compounded and sulfur vulcanized gum stocks do not show a large rise in strength at low degrees of crosslinking. Typical results on SBR 1006 are shown as points in Figure 9.

Apparently, this discrepancy is the result of the different methods of preparation of the vulcanizates. Whereas Taylor and Darin increased M_n for their

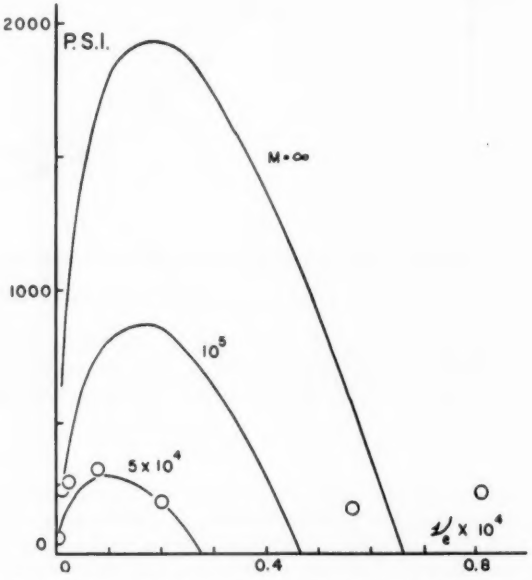


FIG. 9.—Theory curves for gum stocks. The points are for SBR 1006.

rubber by a precipitation procedure, our rubber was not so treated. In addition, our rubber had been milled, and so M_n should be much lower for the rubber used in this work.

The effect of molecular weight on the tensile strength of gum stocks is shown in Figure 9. We have there plotted the tensile strengths predicted by Equation 2 for gum stocks having different values for M_n. The parameters chosen for these theoretical curves and for all the others in this report were $\mathfrak{F}_c = 3.5 \times 10^{-4}$ dyne and a $\mathfrak{F}_c M_0/kT = 10^4$ with M_0 being the average monomer molecular weight.

It is apparent that the theory can be reconciled with the experimental values if one assumes that our milled rubber had an M_n of about 50,000 or less. The curve for $M_n = 100{,}000$ corresponds reasonably well to the data of Taylor

and Darin. These values are in the expected range. The theory wrongly predicts zero strength above a certain critical value of ν_e. This fact has been discussed previously[1]. It is a result of oversimplification of the actual load-sharing mechanism at high degrees of crosslinking.

EFFECT OF FILLER

It is shown in Figures 10 and 11 that the experimental data for SBR 1006 and 1500 containing 30 parts HAF black can be fitted reasonably well with the

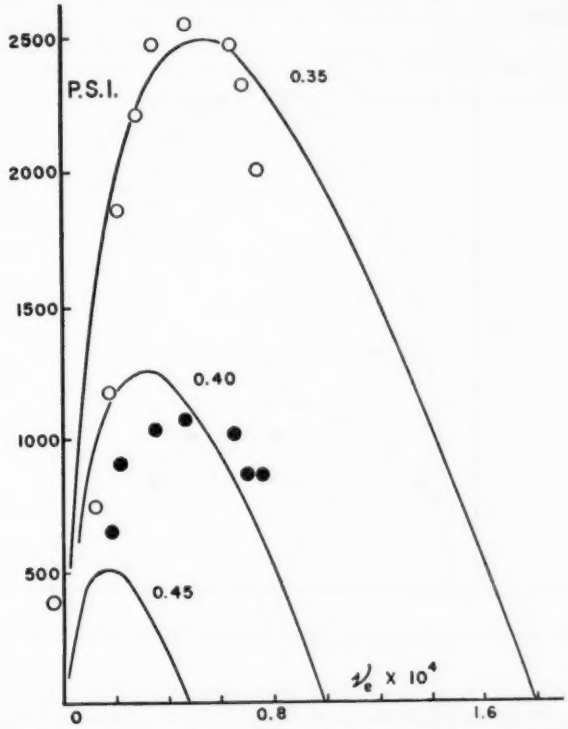


FIG. 10.—Comparison of data for SBR 1006 at 23 and 75° C with the theoretical curves for $M_n = 60{,}000$.

curves predicted by the theory. Of course, now q can no longer be taken as 0.5, since the black particles help to distribute the excess load. It will be noted that q is 0.350 and 0.320 for SBR 1006 and 1500, respectively. The reason for this difference in the q values is not known. However, if the effect is real, it probably means that SBR 1006 does not adhere to the filler as well as does SBR 1500. This may be the result of some impurity in the original stock which tends to coat the filler particles. The data for SBR 1006 loaded with 50 parts

black shown in Figure 4 can be represented by the theoretical relation, provided q is taken to be about 0.28.

The data of Figures 6, 10, and 11 show very clearly that the tensile strength of these vulcanizates decreases markedly at high temperatures. As shown in Figures 10 and 11, this may be interpreted as a change in q with temperature. Since q increases with rising temperature, one is tempted to say that the rubber-filler adhesion bonds decrease in strength or number with rising temperature, thereby nullifying the action of the filler. We believe this to be the case. Of course, at very low temperatures, the rate process involving the slipping of the various chains over each other becomes important[5]. This effect is probably the cause for the low temperature increase in strength observed for the gum stock in Figure 6.

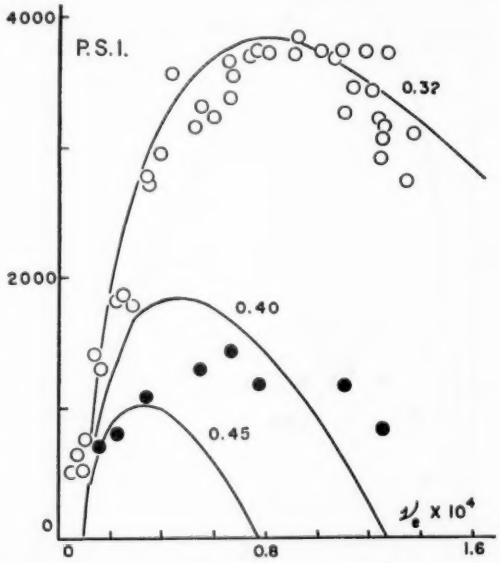


FIG. 11.—Comparison of data for SBR 1500 at 23 and 75° C with the theoretical curves for $M_n = 80{,}000$.

In an effort to study the effect of filler-rubber interaction further, we have examined vulcanizates with two very different fillers. Data for SBR 1006 and 1500 filled with 45 parts calcium carbonate (Calcene TM) are shown in Figure 5. Obviously, this filler is far less effective than HAF black. We interpret this to mean that it is far less strongly bonded to the rubber than is the black. In fact, the data shown for 70° C are not too far different from those for the pure gum stock.

A third filler, Pliolite S-6, was also used. This material is a high styrene-butadiene copolymer which softens at about 60° C. The temperature dependence of SBR 1500 vulcanizates containing 30 and 50 parts Pliolite are shown in Figure 7. It is seen that this material is intermediate between HAF black and Calcene in its effectiveness.

Since it was expected that the Pliolite would vulcanize to the rubber during the curing process, it was rather surprising to notice that no evidence of the softening temperature can be seen in Figure 7. However, a simple calculation indicates that the number of vulcanization bonds at the Pliolite-rubber interface is too small to be of much influence. Apparently the temperature effect is purely an adhesion phenomenon. This is most evident when one considers the temperature dependence of SBR adhesion to Pliolite.

The adhesion test used here was carried out as follows. Pliolite sheets were pressed out at 250° F between carefully cleaned glass plates. The SBR was then pressed out on top of the Pliolite and was vulcanized at 250° F under pressure until the curing reaction in the rubber was essentially completed. We then characterized the adhesion by measuring the force needed to strip the rubber from the Pliolite at a rate of about 2 cm/min under reproducible geometric conditions. This force fell rapidly with increasing temperature, much

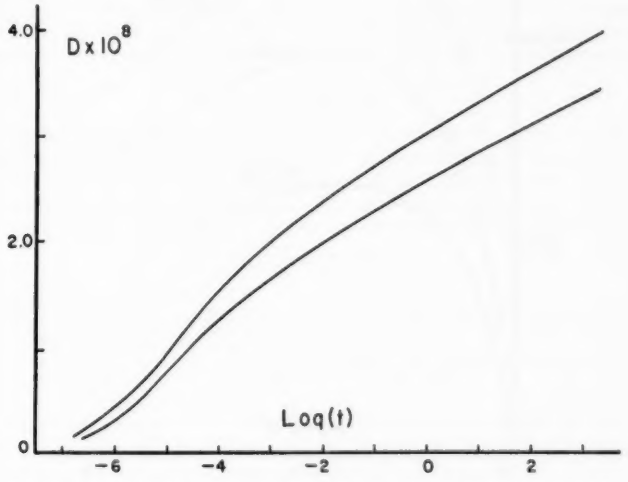


FIG. 12.—Creep compliance curves for stretched and unstretched SBR 1006 containing 30 parts HAF black. Compliance is in cm²/dyne.

as do the tensile strength curves of Figure 7. In addition, poor rubber reinforcing resins such as polystyrene and polymethyl methacrylate showed very poor adhesion under the same test. The adhesion of these materials to rubber was about the same at 25° C as was the Pliolite at 90° C. We tentatively conclude that resins having nearly the same cohesive energy density as rubber will adhere well to it and, consequently, will lead to good reinforcing properties. The adhesion and reinforcing properties decrease rapidly as the difference in cohesive energy densities increases.

As stated previously, it was noted that those vulcanizates containing filler give different values for ν_e depending upon whether the swelling measurements were made on the stretched or unstretched material. This effect is apparently not seriously time dependent, unlike somewhat similar effects noticed in dynamic experiments[6]. It most certainly represents one aspect of the Mullins

effect involving work-softening of filled rubbers. The damage to the rubber from an extensive prestretch is quite apparent in creep curves obtained for samples identical except for prestretching. This is shown by the data of Figure 12 for a vulcanizate containing 30 parts HAF black. One sample had been prestretched to three times its original length and was then allowed to recover for several days before the creep tests were started. The values of ν_e from swelling were 1.28×10^{-4} and 1.40×10^{-4} moles/cc, respectively, for the stretched and unstretched samples. It is interesting to notice that the modulus at long times decreased by a factor which is about equal to the ratio of the two ν_e values.

This decrease in ν_e with stretching seems best interpreted as either (1) a breaking of the most highly strained network chains or (2) a breaking of the

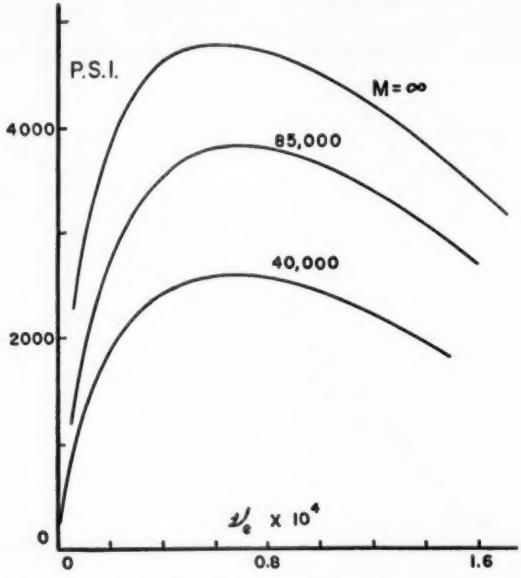


FIG. 13.—Theoretical strength curves for filled rubber having $q = 0.320$.

most highly strained filler-rubber bonds. Consequently, the value of ν_e obtained upon the stretched rubber would appear to be the most closely related to the state of the rubber just before it breaks. We have therefore used these values for ν_e in the figures. Figure 4 indicates that, if the value of ν_e for the rubber near the location of the failure could be obtained, the value of ν_e would actually be zero when the strength is near zero.

EFFECT OF MOLECULAR WEIGHT

Figures 10 and 11 show quite clearly that SBR 1500 is considerably stronger than SBR 1006. This may be explained by the fact that SBR 1500 is known to have a higher M_n than SBR 1006. Indeed, the theoretical relation of Equation (2) predicts the behavior shown in Figure 13. Since the value of the maximum

in the curve is dependent upon both q and M_n, the curves of Figure 13 should not be expected to give exact values of M_n. However, the lower molecular weight of SBR 1006 is almost certainly the cause for its lower tensile strength.

SYNOPSIS

The tensile strengths of high and low temperature SBR rubber vulcanizates containing various fillers have been measured. The fillers used were HAF black, calcium carbonate, and a high styrene-butadiene copolymer (Pliolite S-6). Measurements were made as a function of filler concentration, temperature, and degree of crosslinking. These measurements are compared with the predictions of a molecular theory for tensile strength previously published. The following major conclusions are drawn. (*1*) The theory previously presented for the tensile strength of rubbers is correct in general concept. (*2*) The increase in strength of GR-S with added filler is a result of the fact that the filler particles distribute more widely the additional load imposed when a chain breaks. (*3*) In order for the filler to be effective, the polymer chains must adhere well to its surface. (*4*) The decrease in effectiveness of fillers at high temperatures is a direct result of the poorer adhesion at higher temperatures.

ACKNOWLEDGMENTS

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REFERENCES

[1] Bueche, F., *J. Polymer Sci.* **24**, 189 (1957).
[2] Krause, G., *Rubber World* **135**, 67, 254 (1956).
[3] Flory, P. J., "Principles of Polymer Chemistry", Cornell Univ. Press, Ithaca, New York, 1953.
[4] Taylor, G. R., and Darin, S. R., *J. Polymer Sci.* **17**, 511 (1955).
[5] Bueche, F., *J. Appl. Phys.* **26**, 1133 (1955).
[6] Gehman, S. D., and Clifford, A. M., *Am. Soc. Testing Materials*, Publ. No. **138** (1953); Gui, K. E., Wilkinson, C. S. Jr., and Gehman, S. D., *Ind. Eng. Chem.* **44**, 720 (1952).

THE INFLUENCE OF TEMPERATURE ON THE KINETICS OF CUT GROWTH IN VULCANIZATES *

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Recently published[1–4] research has conclusively demonstrated that rupture in vulcanizates represents a process which increases with time. Slow and fast stages of rupture were discerned[1]. Through the use of high speed photography it was found that, in the usual testing of tensile strength, the rate of rupture growth is initially very small but then quickly although intermittently increases. This behavior occurred both in the rupture of specimens which were not cut and in testing specimens that had been previously cut. The effect of a cut has been thoroughly investigated[5]. Studies conducted on the mechanism of rupture in elastomers indicate that the rupture of vulcanizates has much in common with that of brittle solids. Nevertheless there is a significant difference in the mechanism of rupture in elastomeric materials and brittle solids. It was natural, therefore, to expect a significant change in the kinetics of rupture growth in the region of the glass transition temperature. The aim of the present investigation was to follow the change in the kinetics of rupture of vulcanizates through the transition from the rubbery to the glassy state.

EXPERIMENTAL METHOD

The work was carried out on filled vulcanizates of: (No. 1) SKB (polybutadiene) and (No. 2) a 4:6 mixture of SKB and natural rubber. Compound No. 1 contained 45 per cent carbon black while Compound No. 2 contained 10 per cent. All mechanical testing was done on the dynamometer model TsMG and T, which could be used to test vulcanizates down to temperatures of $-57°$. The problem presented in this investigation required a selection of a suitable sample form so that the growing cut would traverse a significantly large path in the sample and that it would be possible to study the change in the rate of rupture in the course of this process. The samples were rectangles 60 mm long, 50 mm wide, and 2 mm thick. The point of rupture was fixed by placing a 1 mm cut on the operating portion of the sample. At the place where the cut was made, a white line was drawn perpendicular to the direction of the applied stress. The rupture is propagated along this line and a widening of the line indicates additional orientation of the material. High speed photographs were made with a 16 mm SKS camera through the glass door of the thermostatic apparatus. The determination of the rate of exposure was made with a MN-7 type neon time marker. By projecting the resulting moving pictures at the normal speed of 16 frames per second or 24 frames per second it was possible to observe the pictures slowed down 10 to 500 times depending on the speed at which they were taken. In this manner it was possible to carry out widely intermittent measurements with high precision.

* Translated for Rubber Chemistry and Technology by Robert L. Dunning from The Chemistry and Chemical Technology Section of *Nauchnye Doklady Vysshei Shkoly*, No. 2, pages 365–368 (1958).

Using the method described above, the dependence of cut growth on the temperature of testing and the rate of deformation was successfully studied. Over 300 high speed moving pictures were taken and analyzed. From an examination of the results obtained, it was found that for all temperatures used in the study, the reference mentioned earlier[5] describes the functionality of the kinetic curves of rupture. Initially the rate of rupture was so small that it could not be studied with high speed photography. Just prior to the termination of the rupture the rate of rupture growth intermittently increased. The maximum value of the rate of rupture growth at other various conditions was determined at the temperature of testing. By reducing the temperature from 22 to 0° the value of the maximum rate of rupture growth is decreased from 2500 to 1000 mm per second. By further lowering the temperature the rate of rupture growth is decreased still further and then, by reducing the temperature to −50° and lower, the rate of rupture growth again increases reaching a value of nearly 3000 mm per second.

Such a dependence of the maximum rate of rupture growth on temperature was observed on testing SKB vulcanizates (Compound No. 1). The maximum value of the rate of rupture growth is changed unmonotonously by reducing the

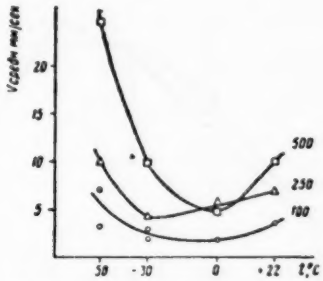


FIG. 1.—The influence of temperature on the mean rate of rupture (ordinate, mm/sec) at strain rates of 100, 250, and 500 mm/min.

temperature from 25 to −50°. The temperature dependence of the rate of rupture growth is determined to some extent by the rate of deformation. From the resulting experimental data it was found that an increase in the rate of deformation generally is accompanied by a displacement of the kinetic curve of rupture growth in the direction of a higher temperature. The statistical nature of rupture of vulcanizates is the reason for some (relatively little) scattering of the maximum values of the rupture growth rate. The value of the mean rupture growth rate is changed much more regularly. In Figure 1 is depicted the dependence of the mean rupture growth on temperature at various rates of deformation. From examining the data presented in this figure, it can be seen that the mean rupture growth rate also is changed unmonotonously by decreasing the temperature and that the temperature curve of the mean rupture growth rate is displaced toward a higher temperature by increasing the rate of deformation.

Such a change of the kinetics of rupture growth with temperature apparently is associated with the transition from elastomeric to brittle solid rupture. Naturally a decrease in the effect of the additional orientation of the vulcani-

zate at the point of rupture growth from a reduction in temperature and a loss of elastomeric behavior by the vulcanizate was expected. This effect was successfully followed and evaluated by comparing the width of the line drawn lengthwise in the direction of the rupture growth, directly at the point of rupture growth d_r and in the untorn portion of the sample d_n. Because of the small difference between the stress at the point of the growing rupture and the stress in the sample, the effect of additional orientation is very slight. As the rupture growth rate increases and surpasses the relaxation rate, which aids in dissipating the excess stress at the point of rupture growth, the excess stress grows and the effect of additional orientation increases. At a temperature of 22° and a deformation rate of 250 mm per minute the ratio of d_r/d_n reached a value of 2.3. By lowering the temperature the final value of d_r/d_n was decreased and at the temperature of $-50°$ it was found to equal 1.2. Of course, it may be that the change of the kinetics of rupture growth detected by us does not reflect the mechanical characteristics of vulcanizates, or more correctly, the characteristic rupture of the vulcanizate.

Isotherms of the deformation of the vulcanizates No. 1 and No. 2 were determined in the range of temperatures studied. In all of the cases studied,

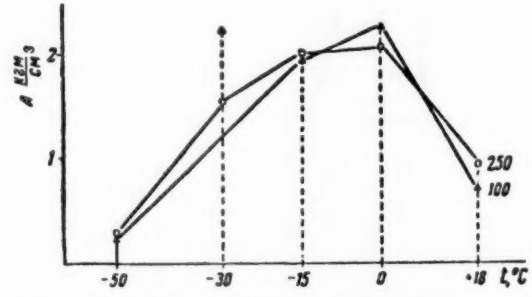


FIG. 2.—The influence of temperature on the value of the work of deformation up to break (ordinate, A kg/cc) at rates of strain of 100 and 250 mm/min.

a reduction in the test temperature was accompanied by a decrease in the relative elongation at break. Earlier Gul and Farberova indicated[6] that the dependence of the relative elongation at break on temperature is determined by a complicated relationship by which there is an opportunity, in principle, for an increase in the relative elongation at break with a decrease in temperature.

As has been shown, the dependence of the relative elongation at break on temperature is determined by the influence of temperature on the tensile strength, described by the equation of Gul[7] or the empirical equation of other authors[1,2,9], and the influence of temperature on the properties of deformation of the material. An unmonotonous change of the relative elongation at break by a reduction in temperature is possibly similarly detected in several cases of unmonotonous change in tensile strength with a change of intermolecular interaction. However, in the peculiar case under question we only observed a monotonous change of the relative elongation at break, although the value of the tensile strength was changed unmonotonously. Characteristically, the presence of a maximum in tensile strength is the result of attaining a temperature at which the rate of rupture growth is markedly reduced.

From an analysis of the temperature dependence of the relative elongation at break and the temperature dependence of tensile strength, it is possible to come to the conclusion that the work of deformation up to break must change unmonotonously with a reduction of temperature. A determination of the value of the work of deformation up to break from the deformation isotherm shows that a reduction of the temperature from 22–16° to 0° is accompanied, as a rule, by an increase in the work of deformation up to break. After reaching a sufficiently low temperature the value of the work of deformation up to break begins to increase again.

In Figure 2 is depicted the dependence of the work of deformation up to break on temperature, obtained from deformation isotherms of SKB vulcanizates with different rates of strain. In a comparison of Figures 1 and 2 it can easily be seen that in the temperature region characterized by a decrease in the rate of rupture, an increase in the value of the work of deformation up to break takes place. A reduction of temperature is accompanied by an increase in the number of intermolecular bonds, which are overcome in the process of deformation and break. This takes place in the region of the elastomeric state. In the process of cooling, the mobility of the molecular chain segments is reduced and the number of intermolecular bonds, which are broken during the process of deformation and rupture, is diminished. The deformation of material in the glassy state is not accompanied by a rupture of intermolecular bonds. However, in the region of the transition from the elastomeric to the glassy state there is a reduction of the value of the work of deformation up to break.

Thus the transition from the elastomeric to the glassy state is accompanied by a decrease in the rate of rupture growth, the value of the relative elongation at break, the tensile strength, and the work of deformation up to break. The determination of these mechanisms has a significant meaning in the resolution of several practical questions connected with the mechanism of rupture in vulcanizates.

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REFERENCES

[1] Bartenev, G. M., *Uspekhi Khim.* **24**, 7, 815 (1955).
[2] Zhurkov, S. N., and Narzulayev, B. N., *Zhur. Tekh. Fiz.* **23**, 10, 1677, (1953).
[3] Späth, W., "Beitrage zur Technologie der Hochpolymeren, Gummi and Kunstoffe", Stutgart, 1956.
[4] Gul, V. E., and Krutetskaya, G. P., *Doklady Akad. Nauk SSSR* **114**, 973 (1957).
[5] Gul, V. E., Krutetskaya, G. P., and Kovpiga, V. V., *Kauchuk i. Rezina* (1957) (Translator's note, no volume or page was given).
[6] Gul, V. E., and Farberova, I. I., *Kolloid. Zhur.* **18**, 660 (1956).
[7] Gul, V. E., *Doklady Akad. Nauk SSSR* **96**, 953 (1954).
[8] Gul, V. E., Fedukin, D. L., and Dogadkin, B. A., *Kolloid. Zhur.* **15**, 11 (1953).
[9] Dodagkin, B. A., and Sandomirskiĭ, D. M., *Kolloid. Zhur.* **13**, 267 (1951); RUBBER CHEM. & TECHNOL. **25**, 50 (1952).

WANDERING OF CROSSLINKS IN RUBBER AT HIGH TEMPERATURE *

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INTRODUCTION

There are strong reasons to believe that on heating a crosslinked rubber crosslinks are broken and new ones formed. This has been established by the well-known work on stress relaxation of Tobolsky and his school, and others[1]. In the following we will discuss some experiments which give further support to these views, both of a qualitative and quantitative nature.

In the first place, we carried out a few preliminary experiments on stress relaxation at elevated temperatures. This stress relaxation may be due to either or both of two effects: (*a*) a displacement of the crosslinks, (*b*) a change in the number of crosslinks per unit of volume (crosslinking density ρ). A measure of ρ can be obtained from the equilibrium degree of swelling at room temperature, and this gives us a means of comparing changes of ρ in a stretched sample with those occurring in the unstretched state. To this end commercial rubber strips were heated in the stretched state in the absence of oxygen at three different temperatures (80, 106, 122° C) for times varying from 2 to 72 hours. The degree of stretch, i.e., the length of the stretched rubber divided by the original length was $\alpha = 1$ (unstretched) in one series, and $\alpha = 3$ in a second series. The initial stress τ_0 (for $\alpha = 3$) and the final stress τ at the end of the heating period were read from the stress-strain diagrams, taking into account that for the heat-treated strips there was a permanent set. In other words, τ is the stress needed to give the heat-treated sample at room temperature a length 3 times the length of the original untreated sample; the ratio τ/τ_0 is therefore essentially the ratio between the moduli of elasticity. The crosslinking densities ρ_0 and ρ before and after heating were derived from swelling experiments (for details see the sections on swelling).

Table I shows that in the unstretched samples the density of the crosslinks at first increases slightly, but subsequently decreases. The initial increase may be due to a certain amount of after-cure: no attempts were made in these preliminary experiments to free the rubber from remnants of sulfur or initiators before heating took place. The subsequent decrease in ρ is probably best explained by degradation.

A comparison of ρ/ρ_0 for $\alpha = 1$ with that for $\alpha = 3$ reveals that stretching at elevated temperatures favors crosslinking. This may be explained by the assumption that the number of positions favorable to crosslinking is increased as a result of stretching.

The most interesting comparison, however, is that between ρ/ρ_0 and τ/τ_0 for $\alpha = 3$, which shows that the modulus of elasticity may decrease in spite of an increase in ρ. This shows conclusively that crosslinks are broken and re-formed.

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It shows, moreover, that great caution is needed when calculating changes in ρ from changes in stress alone as is sometimes done in kinetic studies.

For a more quantitative interpretation of these results, more experiments would have to be done under well-controlled conditions. In view of the fact that several factors may contribute to the final result in an unknown manner, and the interpretation is complicated by the fact that the stretched network is not isotropic, we have preferred to attack the problem in a different way. This is based on the following considerations.

When rubber is crosslinked in solution, it is reasonable to assume that the "normal" coiling of the rubber molecules which exists in the solution before vulcanization is maintained upon crosslinking. The coiling of the network chains (between crosslinks) of the swollen network which is the result of such a process is then said to be "normal". Upon drying without introducing new crosslinks, the resulting gel consists of chains in which the degree of coiling has become "super normal": the crosslinks are closer together, but the number of statistical chain elements between the crosslinks has remained the same as before drying.

TABLE I

CHANGE OF DEGREE OF CROSSLINKING ρ AND OF STRESS τ IN VULCANIZED RUBBER WITH TEMPERATURE AND TIME OF HEATING; α_p = PERMANENT SET

Temperature, °C	Time, hours	ρ/ρ_0 $\alpha=1$	ρ/ρ_0 $\alpha=3$	τ/τ_0 $\alpha=3$	α_p
20	—	1.00	1.00	1.00	1.00
80	24	1.06	1.25	0.64	1.50
	72	1.01	1.14	0.58	1.59
106	2	1.04	1.12	0.72	1.37
	20	0.85	0.92	0.54	1.66
	52	0.60	0.72	0.53	1.68
122	2¼	0.89	1.07	0.57	1.62
	5	0.87	0.96	0.58	1.59
	48	0.35	0.40	0.47	1.81

In the following the volume of a gel divided by that of the dry rubber will be called degree of swelling and will be denoted by the letter q. The equilibrium degree of swelling q_1 of a supercoiled network will be higher than that of a normal network with the same density of crosslinks: the topologies of these two networks are different.

If this is ture, we can predict what will happen when a "supercoiled" network is heated. Any newly formed crosslink which replaces a broken one will link together two chains at positions which are normal for a dry rubber. The average distance between two crosslinks will then be the same as in a network with the same average chain-length but formed in the dry state. In other words, the degree of coiling in the dry state has become "normal." The resulting rubber network will then show a lower equilibrium degree of swelling ($q_2 < q_1$) than the original "supercoiled" network, in spite of the fact that the number of crosslinks per unit volume is the same.

These ideas have been tested quantitatively by comparing experimental values of q_2 with those calculated from q_0 and q_1, where q_0 is the degree of swelling of the initial gel, i.e., the reciprocal of the volume fraction of rubber in the solution in which crosslinking took place.

THEORETICAL

The calculation of q_2 from q_1 and q_0 may be based on two slightly different theories. The one is due to Hermans[2]. For the partial molecular free energy of the solvent in a supercoiled network with a degree of swelling $q_1 = 1/v_1$, this author finds:

$$\partial F/\partial n = kT[\ln (1 - v_1) + (1 - 1/N)v_1 + \gamma v_1^2 + v_1^{\frac{1}{3}}/Nq_0^{\frac{1}{3}}] \qquad (1)$$

in which N represents the number of statistical chain elements between crosslinks, γ is the Huggins' interaction constant, k is Boltzmann's constant, and T is the absolute temperature. The arbitrary constant in the expression for $\partial F/\partial n$ has been so chosen that $\partial F/\partial n$ is zero when the rubber concentration is

TABLE II

SWELLING IN BENZENE AT ROOM TEMPERATURE FOR HEAT-TREATED RUBBERS VULCANIZED IN SOLUTION

No.	q_0	q_1	q_2, expt.	q_2 calc. Hermans	q_2 calc. Flory
A	1	10.96	10.96	10.96	10.96
B	1	8.60	8.55	8.60	8.60
C	1	8.70	8.67	8.70	8.70
D	1	7.51	7.56	7.51	7.51
E	1	7.41	7.56	7.41	7.41
1	3.58	20.95	12.6	12.4	12.9
2	3.58	20.00	11.7	11.7	12.1
3	3.00	16.90	10.6	10.7	11.1
4	2.75	14.51	10.0	9.6	10.0
5	3.28	13.85	9.5	8.4	8.9
6	3.19	14.32	9.6	8.8	9.4
7	8.99	41	16.5	15.9	17.2
8	9.98	49	17.0	18.1	19.6

zero. Consequently, the condition for equilibrium with the pure solvent is: $\partial F/\partial n = 0$. This gives, after expanding $\ln (1 - v_1)$:

$$N = \frac{q_1[(q_1/q_0)^{\frac{1}{3}} - 1]}{(\frac{1}{2} - \gamma) + (1/3q_1) + (1/4q_1) + \ldots} \qquad (2)$$

Thus, N may be calculated from the volume fraction of rubber in the solution in which crosslinking took place ($v_0 = 1/q_0$) and from the equilibrium degree of swelling q_1 of this crosslinked rubber. After heating, the supercoiled network has become "normal," and the equilibrium degree of swelling q_2 will obey the equation:

$$N = \frac{q_2(q_2^{\frac{1}{3}} - 1)}{(\frac{1}{2} - \gamma) + (1/3q_1) + (1/4q_1) + \ldots} \qquad (3)$$

Eliminating N from Equations (2) and (3), one finds the desired relationship between q_2, q_1, and q_0.

On the other hand, according to Flory[3], one has in a network with a functionality f:

$$N = \frac{q_1[(q_1/q_0)^{\frac{1}{3}} - 2/f]}{(\frac{1}{2} - \gamma) + (1/3q_1) + (1/4q_1) + \ldots} \qquad (2')$$

and a similar expression to replace Equation (3).

For the calculation of q_2 from experimental values of q_1 and q_0, with $\gamma = 0.42$[4], we used both expressions (the latter one with $f = 4$). They lead to values of q_2 which are different from each other. The experimental results are not in favor of either one of these theories in particular, however, as may be seen from Table II.

EXPERIMENTAL

VULCANIZATION

Vulcanization in solution was achieved by mixing a solution of rubber, zinc dibutyl dithiocarbamate, and dibenzylamine in benzene with an equal volume of a solution of rubber and sulfur in benzene. Vulcanization occurred upon standing for at least 1–2 days at room temperature. Gels with different q_0 and q_1 values were obtained by changing the concentrations of ingredients and/or the time of vulcanization, as deduced from preliminary experiments. Gels A-E were prepared by evaporation of the solvent immediately after mixing of the two solutions.

SWELLING EXPERIMENTS

The samples listed in Table II were put in weighing bottles and swollen in benzene in the dark. The swollen gel was dried in the dark at room temperature and reswollen in benzene. The drying and swelling was repeated several times in order to remove any soluble matter from the networks. The swelling time was such that the volume of the gel afterwards increased no more than 10% per 100 hours. The equilibrium degree of swelling was found, as is done by most authors[5], by extrapolating back the linear part of the swelling volumes vs. time curve to zero time, a procedure which may be inaccurate for large degrees of swelling (samples 7 and 8, Table II). The degree of uncertainty is considerably smaller for the other experiments. In later swelling experiments, the rate of fractional uptake of benzene, and thus the swelling time for a given gel, was found to be dependent upon the form and size of the original gel; this may be expected for a process which is mainly governed by diffusion of the swelling medium into the gel.

HEAT TREATMENT

The swollen gels were dried at room temperature and heated at 100° C in a glass tube first filled with nitrogen and then connected with a Leybold oil pump. After a few hours of heating, the rubber was swollen in benzene at room temperature and the degree of swelling was determined. By repeating this process several times, the degree of swelling was found to decrease with time of heating, approaching a limit at time $t = \infty$, which was found by plotting q against $1/t$ and extrapolating linearly to $1/t = 0$. There are the values of q_2 listed in Table II.

No such decrease was found in parallel experiments in which the gels were kept for the same time at room temperature, rather than at 100° C.

RESULTS AND DISCUSSION

The experimental and calculated degrees of swelling are compiled in Table II, in which the first column gives the number of the sample. q_0 represents the reciprocal of the volume fraction of rubber at which vulcanization took place; in other words, the concentration varied between 10 and 100%. Samples A-E

are normal coiled in the dry state; samples 1–8 in the dry state are "supercoiled" networks. The next column (q_1) gives the equilibrium degree of swelling before heating; the heating itself took place in the dry state. The experimental value of q_2 (degree of swelling measured after heating extrapolated to infinite heating time) is listed together with the values of q_2 calculated by either of two methods (Hermans[2] or Flory[3], see Theoretical part) in the last three columns. (The calculated values of q_2 are only slightly dependent on the value of the interaction constant γ; moreover, γ does not depend strongly on the concentration of rubber[5].

The vulcanization conditions have been varied in such a way as to cover a broad range of degrees of swelling. It is seen from Table II that agreement between theory and experiment is satisfactory.

One might argue that this result could be explained equally well by assuming that *additional* crosslinks are formed in the heating process, so that the total number of crosslinks after heating is larger than before. However, this is ruled out by the fact that rubbers which have been crosslinked in the dry state (samples A-E) do not show any appreciable change in the number of crosslinks when heated under the same conditions.

The problem is obviously of considerable interest, because the results show that a rubber network is not uniquely defined by the number of crosslinks per unit of volume. One must distinguish between what may be called different "topologies" of a network. Furthermore, the very fact that no further crosslinks are formed, although crosslinks are broken and reformed at other spots, is very suggestive. One is inclined to conclude that a new crosslink can be formed only from some remnant of a broken one, as in the stress relaxation experiments.

SYNOPSIS

By crosslinking natural rubber in benzene, networks are prepared in which the degree of coiling is higher than normal ("supercoiled" networks). On heating, these networks are converted to normal ones with the same number of crosslinks but a lower degree of equilibrium swelling. The results of the swelling experiments are in quantitative agreement with theoretical predictions. Results of stress relaxation experiments at elevated temperatures support the conclusion reached on the basis of swelling. It follows that great caution is needed when calculating changes in the density of the crosslinks from changes in stress alone as is sometimes done in kinetic studies.

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REFERENCES

[1] For example, Berry, J. P., Scanlan, J. and Watson, W. F., *Trans. Faraday Soc.* **52**, 1137 (1956).
[2] Hermans, J. J., *Trans. Faraday Soc.* **43**, 591 (1947).
[3] Flory, P. J., *J. Chem. Phys.* **18**, 108 (1950).
[4] Gumbrell, S. M., Mullins, L. and Rivlin, R. S., *Trans. Faraday Soc.* **49**, 1495 (1953).
[5] Gee, G., *J. Chem. Soc.* **1947**, 280.
[6] Bueche, A. M., *J. Polymer Sci.* **15**, 97 (1955).

OIL EXTENDED STYRENE-BUTADIENE RUBBER SKS-30M *

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Serious difficulty has been encountered by the rubber industry in the use of oil filled (oil extended) styrene-butadiene rubbers made by high temperature polymerization because of their poor properties. Thus, unsatisfactory results were obtained in processing samples of SKS-30M prepared in the Voronezh synthetic plant during 1955–1956. As a consequence, production of the rubber by that organization has been delayed a few years. This paper briefly presents progress and results of work undertaken for the purpose of improving the properties of styrene-butadiene rubber, SKS-30M.

The above mentioned samples of Voronezh plant SKS-30M were produced from latex that was prepared without the use of a polymerization modifier. The hardness of the rubber before extending with oil was nearly 6000 g. (Translator's note: there is no explanation of the hardness term used or its units. It is probable, however, that this is a plasticity value similar to Defo, and that the units are grams.) It is known that physical properties and especially technological (processing) properties of SKS-30M made with unmodified rubber are worse than those obtained with modified rubber. Therefore it was supposed that the difficulty arising from the use of high temperature polymerized oil extended rubber in factories was a result of omission of modifier from the polymerization recipe.

The omission of modifier from the process was at one time dictated by the desire to obtain a tough rubber which could be easily dried, thus permitting the introduction of the largest possible quantity of mineral oil. On a theoretical basis it was expected that the introduction of a considerable quantity of lubricating oil 18 would result in production of a rubber with normal processing properties. However, experiments did not confirm the expected results. Therefore the purpose of these tests is to demonstrate the possibility of improvement of the properties of SKS-30M rubber by using modifiers in the latex preparation.

The experiments showed that the properties of oil extended styrene-butadiene rubber SKS-30M are considerably improved if modified latex is used for its preparation. SKS-30M rubber obtained from the modified recipe contains considerably less gel (45%) than the unmodified (87%), and has a hardness of 3000–4000 g. It is known that an increase in gel content causes poorer processing properties of rubbers. In addition, the physical properties of modified SKS-30M are somewhat higher (Table I).

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TABLE I

CHARACTERISTICS OF THE POLYMERIZATION PROCESS AND PROPERTIES OF THE RUBBERS OBTAINED *

Property	Latex obtained: With modifier	Latex obtained: No modifier
Reaction time, hours	16.8	17.1
Monomer conversion, %	58.3	57.0
Rate of reaction, % of control	100	97.8
Properties of latex		
Surface tension, dynes/cm	37.0	36.9
Quantity of coagulum formed in polymerization process, % of rubber	0.16	0.35
Formation of coagulum on 100 fold dilution with water	none	none
Properties of rubber		
Solubility of rubber in toluene, %	55.0	13.1
Hardness before plastication, g	3713	6230
Hardness after plastication, g	1068	1442
Tensile strength, kg/cm²	268	264
Relative elongation, %	618	608
Residual elongation, %	22	21
Modulus at 300% elongation, kg/cm²	81	86
Elastic rebound, %	40	42

* The polymerization process proceeds at the same rate and with the same kinetics with and without modifier. Omission of modifier from the process resulted in less stability of the polymerization system; more coagulum formed. Physical properties of the rubber were determined by GOST 6074-51. Latex properties methods are described by V. N. Relkh and V. A. Fainberg.

Comparison of oil extended rubbers prepared from modified and unmodified latexes favors the rubber made from the modified product (Table II).

Vulcanizates made from oil extended modified rubber containing 15% lubricating oil 18 and having a hardness of 3000–4000 g have greater tensile strength and higher relative elongation than those prepared from unmodified oil extended rubber. Elasticity and residual elongation are of the same order for both rubbers.

TABLE II

PHYSICAL PROPERTIES OF RUBBERS EXTENDED WITH 15% OIL

Property	Rubber: From modified latex	Rubber: From unmodified latex
Surface tension of the latex, dynes/cm	36.9	37.3
Rubber content of latex, %	31.5	31.0
Hardness of original rubber, g	3877	6484
Properties of SKS-30M-15 rubber		
Hardness before plastication, g	2077	3430
Hardness after plastication, (thermal), g	250	233
Vulcanization time, minutes	80	80
Tensile strength, kg/cm²	252	243
Relative elongation, %	592	544
Residual elongation, %	19	16
Modulus at 300% elongation, kg/cm²	83	89
Elastic rebound, %	34	35

TABLE III

CHARACTERISTICS OF RUBBERS OF DIFFERENT ORIGINAL HARDNESS EXTENDED BY DIFFERENT AMOUNTS OF LUBRICATING OIL, 18

Extension by oil 18, %	Hardness of rubber SKS-30 before plasticization, g	Hardness of rubber SKS-30 after oil addition, g	Hardness of thermoplasticated rubber, SKS-30M, g	Optimum vulcanization time, minutes	Tensile strength, kg/cm²	Relative elongation, %	Residual elongation, %	Modulus at 300% elongation, kg/cm²	Elasticity on rebound, %
0	3000–4000	—	—	92	268	653	21	75	41
15	3000–4000	1454	239	69	242	616	16	75	38
20	3000–4000	1280	200	78	236	619	17	69	36
25	3000–4000	1007	190	76	221	612	18	71	36
0	2000–2500	—	—	82	285	657	24	82	35
15	2000–2500	1115	200	88	252	620	19	80	31
20	2000–2500	817	200	82	231	609	20	78	30
25	2000–2500	596	200	92	221	607	21	78	28
30	2000–2500	385	200	90	209	636	24	70	29
0	1000–1500	—	—	92	272	676	25	70	34
15	1000–1500	714	200	83	237	607	22	80	31
20	1000–1500	499	200	85	221	601	26	78	29
25	1000–1500	357	200	91	215	614	27	73	28
30	1000–1500	300	—	85	204	656	28	65	27

Oil extended modified rubber, SKS-30M-15, is soft and quickly plasticated. Extending rubbers with lubricating oil 18 (15%) causes some decrease in some of the physical properties as compared with plasticated SKS-30 rubber; but the decrease is of the same order as obtained when low temperature (cold) rubber, SKS-30A, is extended with the same quantity of oil. No more than 15% lubricating oil 18 should be added to SKS-30 of hardness 3000–4000 g because larger quantities cause a noticeable decrease in strength of the vulcanizates. On extending with 25% oil the strength of the vulcanizates decreases by 15–20% and the hardness drops to 1000 g (Table III).

TABLE IV

CHARACTERISTICS OF EXPERIMENTAL SKS-30M-15

Property	Produced, 1957			Produced, 1955
	Sample 296	Sample 297	Sample 298	Sample 529
Oil content of rubber, %	14.3	15.7	15.5	17.6
Hardness of SKS-30M-15 rubber before plastication, g	2500	2500	2300	2900
Hardness of SKS-30M-15 rubber after thermoplastication, g	below 200	below 200	below 200	below 200
Moisture content, %	1.0	0.1	0.1	—
Fatty acid content, %				
Free	1.22	1.33	1.26	1.97
Bound	0.17	0.34	0.25	—
PBNA * content, %	2.45	2.35	2.30	2.73
Ash content before dusting, %	0.26	0.36	0.25	0.30
Ash content after dusting, %	2.62	3.3	3.2	1.63
Time of plastication to reach hardness of 1000 ± 100 g, minutes	8	8	7	—
Vulcanization time, minutes	80	60	60	100
Tensile strength, kg/cm²	272	273	282	253
Relative elongation, %	645	550	642	543
Residual elongation, %	24	20	24	18
Elastic rebound, %	40	37	36	39

* Phenyl-2-naphthylamine.

Addition of lubricating oil 18 to SKS-30 rubbers with hardness of 2000–2500 g and of 1000–1500 g produces similar changes. 15% oil added to 2000–2500 g hardness rubber drops the hardness to 1000 g. Preliminary plastication can be omitted on this rubber. Little increase in plasticity can be achieved in the rubber mixer by adding plasticating agents.

Because of the desire to obtain rubber which needs no plastication, the producers tested rubbers modified to hardness of 2000–2500 g by increasing the amount of oil above 15%. 30% oil was required to decrease the hardness to 400 g. Such a level is not suitable since the physical properties of the rubber become considerably worse.

It was established that in order to solve the problem of obtaining SKS-30 rubber which needs no plastication and which contains 15% oil it is necessary to decrease the initial rubber hardness to 1000–1500 g. Then extending with 15% oil lowers the hardness to 400–700 g.

In accordance with the laboratory data and with the recommendations of VNIISK, in October, 1957, the Voronezh factory with the assistance of scientists from VNIISK, prepared industrial experimental samples of oil extended butadiene styrene-rubber, SKS-30M-15, 14–17% oil extended, from high temperature, modified latex. The production of the experimental samples gave no difficulties in the emulsion polymerization plant or in the coagulation plant. Productivity of the equipment did not decrease in any section of the factory. The characteristics of the experimental sample of SKS-30M-15 are given in Table IV.

Preparation of rubber products from the experimental rubber samples in the Voronezh tire plant met with no difficulty thus leading to the opinion that SKS-30M-15 can be used for manufacturing automobile tires.

The samples of SKS-30 latex were prepared by the following laboratory and factory recipe, given in parts by weight:

Butadiene	70
Styrene	30
Water	100
Nekal, 68% purity	3.7
Synthetic fatty acid (C_{10}–C_{16} fraction)	0.7
Caustic soda	0.35
Potassium persulfate	0.45
Isopropylxanthogen disulfide or ethylxanthogen disulfide	0.08

The polymerization was conducted at 50° to a conversion of 60%. The modifier (alkylxanthogen disulfide) was omitted from unmodified latex. (Translator's note: For comparison it is of interest to reprint the recipe first used for the production of Government rubber, GR-S, in the United States, known as the Mutual Recipe.)

THE MUTUAL RECIPE

Ingredient	Weight parts
Butadiene	75
Styrene	25
Water	180
Soap	5.0
Lorol mercaptan (C_{12} average)	0.5
Potassium persulfate	0.3

Polymerization was conducted at 50° for 12 hours to 75% conversion.)

The emulsion of lubricating oil 18 was prepared by the following recipe; quantities in parts by weight:

Lubricating oil 18	100
Synthetic fatty acid (C_{17}–C_{21} fraction)	5.5
Triethanolamine	2.7
Water	141.8

The rubber compound for the determination of physical properties of the oil extended rubber was prepared from the following recipe (weight parts):

	SKS-30M	SKS-30 control
Rubber	100	100
Stearic acid	2	2
Zinc oxide	5	5
MBTS	1.5	0.6
Diphenylguanidine	0.3	0.75
Gas black	50	50
Sulfur	2	2
Rubrax (an asphalt)	—	5

For the preparation of the experimental samples of oil extended SKS-30M-15 the amount of modifier was reduced from 0.08 to 0.04 part. For the oil emulsion, 100 parts of lubricating oil 18 were emulsified with 5 parts of stearic acid, 2.5 parts of triethanolamine and 92.5 parts of water. The oil emulsion was fed into the latex stream continuously so as to obtain 14–17% oil in the rubber.

The measurement of the latex and the oil emulsion streams and the regulation of their proportions was carried out with the apparatus used for SKS-30AM rubber latex preparation, except for a change in the pipe line diameter. Coagulation was carried out with 26% calcium chloride solution and 10% acetic acid containing 0.2% ferrous sulfate. The rubber was dried as follows: first zone, 110–130°; second zone, 110–124°; third zone, 104–112°.

CONCLUSIONS

The results indicate that there is a real possibility of obtaining oil extended SKS-30M-15 rubber with satisfactory physical and processing properties from high temperature, modified latex.

CROSSLINK DENSITY IN POLYBUTADIENE *

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INTRODUCTION

Crosslinks formed during the emulsion polymerization of conjugated dienes are considered to be detrimental to some polymer properties, so that a study of crosslinking appeared to have practical importance as well as theoretical interest. In such systems, the extent of crosslinking at the gel point has been determined[1–3] by a method developed by Morton and Salatiello[1]. The present work describes the measurement of crosslink density in emulsion polybutadiene by an independent method which permits determinations to be made as only one polymerization variable is changed.

Stockmayer[4] has pointed out that, in a crosslinked polymer system, the number of polymer molecules equals the number of primary chains minus the number of crosslinkages. Primary chains are the polymer molecules which would exist if no crosslinking had taken place. This may be expressed as:

$$1/\bar{n}_n = 1/\bar{n}_p - \rho/2 \tag{1}$$

in which $\bar{n}_n$ is the number-average molecular weight of the polymer molecules in monomer molecule units, $\bar{n}_p$ is the number-average weight of the primary chains in monomer molecule units, and ρ is the fraction of the polymerized monomer units involved in crosslinks. The term *crosslink density* is used here as the equivalent of ρ. Osmotic pressure has been used to determine $\bar{n}_n$ while the value of $\bar{n}_p$ has been found by the use of radioactive modifiers or chain transfer agents in the polymerizations and radioactive analysis of the resulting polymer. This procedure assumes that each primary chain contains one and only one modifier fragment. From these data, the crosslink density can be calculated using Equation (1).

EXPERIMENTAL

Three types of radioactive modifiers were prepared and used. The *tertiary alkyl mercaptans* were prepared by the reaction of H_2S^{35} with the appropriate olefin at virtually atmospheric pressure in the presence of aluminum chloride. The distilled products were subjected to potentiometric titration with silver salts to demonstrate their purity. *Primary dodecyl mercaptan* was prepared by the reaction of $NaHS^{35}$ and lauryl bromide. This modifier had uniform radioactivity in distillation fractions. *Diisopropyl xanthogen disulfide* was prepared by the hypochlorite oxidation of the reaction product of isopro-

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panol-C^{14}, potassium hydroxide, and carbon disulfide. The melting point of this product agreed with the known value.

Polymerizations of butadiene or of styrene were conducted by the soda bottle technique. The materials used were the purest grade available and, generally, no further purification was attempted. Butadiene was of research grade and was distilled immediately before use. Excess butadiene was vented from bottles before capping to remove air, while styrene runs were vented with nitrogen for the same purpose. The following description of recipes does not mention that all contained monomer 100, and variable modifier while the sodium (NaOSR) or potassium (KOSR) Office of Synthetic Rubber soap had specifications listed in the Office of Synthetic Rubber Laboratory Manual 2.3.0.5.1 and 2.3.0.12.1.

Persulfate recipe, 50° C.—H_2O 180; NaOSR soap or potassium myristate 5.0; $K_2S_2O_8$ 0.3. Shortstop 0.2 hydroquinone.

Persulfate recipe, 5° C.—H_2O 180, KOSR soap 5.0; $K_2S_2O_8$ 0.3. Shortstop 0.2 hydroquinone.

Dextrose recipe, 50° C.—H_2O 180; NaOSR soap 5.0; cumene hydroperoxide 0.05; dextrose 0.05; $Na_3PO_4 \cdot 12H_2O$ 0.3. Shortstop 0.2 hydroquinone.

Polyamine recipe, 5° C.—H_2O 180; KOSR soap 5.0; Tamol N (sodium salt of condensed aryl sulfonic acid; sold by Rohm and Haas Co.) 0.2; KCl 0.3. Shortstop 0.2 potassium dimethyldithiocarbamate. The amounts of diisopropylbenzene hydroperoxide, diethylenetriamine, and $FeCl_3 \cdot 6H_2O$ were variable.

Polyamine recipe, −18° C.—H_2O 180; methanol 60; potassium oleate 5.0. Shortstop 0.2 potassium dimethyldithiocarbamate. The amounts of diisopropylbenzene hydroperoxide; tetraethlyenepentamine; $FeCl_3 \cdot 6H_2O$, tetrasodium ethylenediamine tetraacetate, and $Na_3PO_4 \cdot 12H_2O$ were variable.

Hydrogen peroxide recipe, 50° C.—H_2O 200; potassium oleate 6.0; H_2O_2 0.06; $Fe_2(SO_4)_3 \cdot xH_2O$ 0.04; $CoCl_2 \cdot 6H_2O$ 0.002; $Na_4P_2O_7$ 1.25. Shortstop 0.2 hydroquinone; or 0.3 hydroquinone plus 0.36 potassium dimethyldithiocarbamate.

Nitrazole recipe, 50° C.—H_2O 200; NaOSR soap 5.0; NaOH 0.3; Nitrazole CF (*p*-nitrobenzenediazonium fluoroborate, sold by General Dyestuffs Corp.) 0.05. Shortstop 0.2 potassium dimethyldithiocarbamate.

Sulfoxylate recipe, 5° C.—H_2O 180, KOSR soap 5.0; diisopropylbenzene hydroperoxide 0.1; sodium formaldehyde sulfoxylate 0.1; $FeSO_4 \cdot 7H_2O$ 0.02; tetrasodium ethylenediamine tetraacetate 0.04; KCl 0.4. Shortstop 0.2 potassium dimethyldithiocarbamate.

To prevent oxidative crosslinking or degradation during purification of the polymer, exposure to air and light was kept at a minimum by the use of opaque apparatus containing a nitrogen atmosphere. The latex from polymerization was added to acidified isopropanol and the resulting floc was washed several times in isopropanol before drying under vacuum. The polymer was then extracted with cold ethanol/toluene azeotrope for at least 24 hours and dried as before. The polymer was dissolved in toluene containing 0.4 g phenyl-beta-naphthylamine/100 ml at the temperature of the osmometers. In subsequent dilution, dialysis, and osmometry of this polymer solution, the solvent used contained this amount of antioxidant, and in calculations of solids content for molecular weight and radioactivity determination, corrections were applied for this amount of phenyl-beta-naphthylamine.

Dialysis of the polymer solution was conducted in a desiccator in which both solution and solvent were stirred magnetically. A cellulose membrane exactly like those used in the osmometers was employed, and a contact area of 120 cm^2

separated 250 cc of the polymer solution and 3500 cc of solvent. The dialysis was continued until constant radioactivity of the polymer was attained which generally required one to two weeks. During this process the solvent was changed at least twice a week.

This extensive purification of the polymer was considered necessary to prevent diffusion of the polymer in the osmometers and thus measure both osmotic pressure and radioactivity on identical portions of the polymer. A loss of 2.5–3.0% of the whole polymer accompanied this procedure.

The radioactivity of the dialyzed polymer was measured by evaporating the solution on a stainless steel disc. The polymer on these dics was smoothed and freed from bubbles by standing overnight covered with toluene in a toluene saturated atmosphere. The radioactivity was determined in an end-window Geiger tube/scaler apparatus and such results, corrected for background, were converted into per cent modifier by comparison with discs holding nonradioactive polymer containing known amounts of modifier. The modifiers in these standard plates were immobilized by oxidation or reaction with chloral. The molecular weight of the modifier and monomer with the per cent modifier were used to calculate $\bar{n}_p$.

The number-average molecular weight of the polymer was determined essentially as described by Sands and Johnson[5]. Three cells each of four concentrations were used and, to correct for membrane sag and minimize errors due to dilution, adjustment was made in the solvent level so that the final position of the solution approximated its original position corrected for pressure. The cellulose membrane used was Sylvania's gel film, gage 450. It had never been dried and was brought into toluene by means of acetone, the day before use in the osmometers. Linear least squares treatment was used to extrapolate the pressure/concentration vs. concentration plot to zero concentration.

RESULTS AND DISCUSSION

Results obtained on polymer prepared at 50° C with tertiary alkyl mercaptan modification are found in Table I and Figure 1. Polystyrene shows a molecular ratio of modifier to polymer of 1.01, which is evidence that the experimental technique is satisfactory. The crosslink density of polybutadiene increases with the molecular weight of the polymer, but at a given molecular weight is independent of conversion, within the range studied, or type of initiation.

The use of modifier analysis to determine molecular weight of the primary chains requires some justification even though modifier attached to the polymer, and not that which has disappeared, is measured here. While chain transfer in the presence of modifier is more frequent than initiation or termination steps, the latter events may have a definite effect on results. With most initiation systems, such as that in the dextrose recipe, or Nitrazole CF recipe, which do not depend on mercaptans for propagation, radicals derived from the initiator, rather than modifier fragments, may be attached to some primary chains. This is especially apparent, if the principal mode of termination is the reaction of two growing chains as proposed by Smith and Ewart[6]. Modifier analysis would indicate a too large average primary chain so that crosslink density results would be low. Results obtained with the Nitrazole CF recipe demonstrate this. The low mole ratio of modifier to polymer in polystyrene indicates that some primary chains do not contain mercaptan modifier, while the indicated crosslink density in polybutadiene is much lower than with other

recipes. If this result were corrected for primary chains containing no modifier, as indicated by the styrene results, the crosslink density would be 5.6 $\times 10^{-4}$, which, considering molecular weight, agrees with persulfate results. On the other hand, the persulfate recipe requires mercaptan to polymerize butadiene, so it is presumed that only modifier fragments may be attached to the polymer. In this case, mutual termination of two growing chains would lead to high crosslink density results. The agreement of crosslink density results from the persulfate and dextrose recipes indicates that initiation and termination steps are not causing a significant error.

The molecular weight of primary chains calculated from modifier content may also be in error if the modifier reacts with the polymer in nonterminal positions. This has been found to occur with primary alkyl mercaptans[7], but tertiary alkyl mercaptans have little or no such tendency. The data of Table I confirm this since longer reaction times (higher conversions) and larger mer-

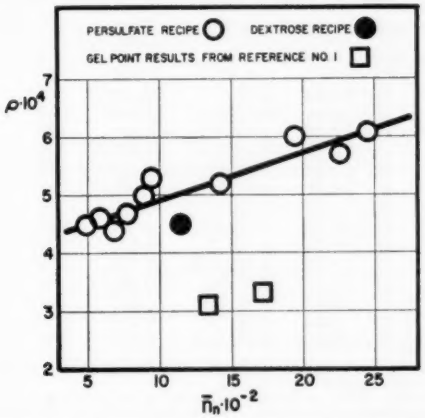


FIG. 1.—The crosslink density, ρ, of polybutadiene prepared at 50° C with tertiary alkyl mercaptan modification vs. polymer molecular weight, $\bar{n}_n$.

captan charges (lower polymer molecular weights) do not increase the calculated crosslink density.

Branching will not be detected by this method if it is considered to be hydrogen transfer as proposed by Flory[8]. The simplest case of branching would show two polymer molecules and two primary chains which, from Equation (1), would indicate no crosslinks. This method does not measure more than one crosslink between two particular primary chains and will not detect the crosslink which results in formation of a cyclic configuration.

In a qualitative way the results of Table I agree with the kinetics of crosslinking as applied to emulsion polymerization by Morton[1] from Flory's original work[8]. It was noted that the monomer-polymer particle in emulsion polymerization is the site of most propagation, and that studies by Meehan[9] had indicated that polymer-monomer concentration ratio in these particles was constant up to 0.52 degree of conversion. It followed then, that the relative rate of crosslinking to propagation should be constant up to that degree of conversion. Subsequent work[10] indicated that the polymer-monomer concentra-

tion ratio in the particle appeared to be dependent on the molecular weight of the polymer, and it was suggested[1] that the relative rate of crosslinking to propagation would increase with changes which increased the molecular weight of the polymer. Figure 1 shows such a relationship.

Gel point crosslink density results[1] obtained on polybutadiene prepared by the persulfate recipe at 50° C with tertiary alkyl mercaptan modification have been placed in Figure 1. The polymer molecular weights of these results have been calculated from the original data by the use of Equation (1) and are for the whole polymer. The gel point method is based on the calculation of the weight-average molecular weight of the primary chains from mercaptan disappearance data using an equation derived by Bardwell and Winkler[11] and the

TABLE I

CROSSLINK DENSITY OF POLYBUTADIENE PREPARED AT 50° C WITH TERTIARY ALKYL MERCAPTAN MODIFICATION

Recipe[a]	Monomer[b]	Kind of modifier[c]	Phm. modifier[d]	α/hrs.[e]	% modifier in polymer	$\bar{n}_p$	$\bar{n}_n$	$\rho \times 10^4$ [f]
Pers.	Sty.	D	0.48	0.55/3	0.512	378	383	(1.01)[g]
	Bde.	O	0.46	0.37/12	0.600	448	498	4.5
	Bde.	O	0.25	0.12/4.5	0.511	526	599	4.6
	Bde.	O	0.26	0.23/8	0.454	593	682	4.4
	Bde.	O	0.40	0.37/12	0.411	655	775	4.7
	Bde.	D	0.41	0.37/10.5	0.514	724	884	5.0
	Bde.	O	0.24	0.39/12	0.360	748	932	5.3
	Bde.	O	0.28	0.42/12	0.259	1041	1422	5.2
	Bde.	O	0.19	0.41/12	0.220	1226	1940	6.0
	Bde.	D	0.21	0.37/10.5	0.272	1372	2253	5.7
	Bde.	D	0.22	0.47/12	0.265	1408	2456	6.1
Dext.	Bde.	O	0.24	0.41/3.5	0.296	911	1145	4.5
Nit.	Sty.	D	0.24	0.35/14	0.204	950	843	(0.89)[g]
	Bde.	D	0.35	0.34/13.5	0.443	841	951	2.8

[a] The kind of recipe described in the experimental section. Persulfate is indicated by Pers., the dextrose recipe by Dext. and the Nitrazole CF recipe by Nit.
[b] Kind of monomer used. Sty. stands for styrene and Bde. for butadiene.
[c] The type of tertiary alkyl mercaptan used. Tertiary octyl mercaptan is represented by O and tertiary dodecyl mercaptan by D.
[d] Parts mercaptan loaded per hundred parts of monomer.
[e] Fractional conversion of monomer to polymer in the indicated hours of polymerization time.
[f] The relation among $\bar{n}_p$ (the number-average molecular weight of the primary chains in monomer molecule units), $\bar{n}_n$ (the number-average molecular weight of the polymer molecules in monomer molecule units), and ρ (the fraction of the polymerized monomer molecules involved in crosslinks or crosslink density) is given in Equation (1). Osmotic molecular weight measurements yield $\bar{n}_n$ values, while % modifier in polymer is used to calculate $\bar{n}_p$.
[g] Styrene results are reported as mole ratio of modifier to polymer.

well-known mathematical probability relation that at the gel point there is a crosslinked monomer unit for every weight-average primary chain. The gel point method, like the method of this paper, assumes that primary chains are defined exactly by the modifier. It will be noted that crosslink density results by the gel point method are smaller than those of this work.

A similar discrepancy was found by Morton et al.[2] in work with polyisoprene. They used ρ obtained from the gel point method and $\bar{n}_p$ from mercaptan disappearance data to calculate the polymer molecular weight using an equation similar to Equation (1). The calculated polymer molecular weight was lower than that obtained by osmometry. They did not think it reasonable to believe that the actual crosslinking could be several times as great as that measured by the gel point method. They believed the cause of the discrepancy was that

TABLE II

CROSSLINK DENSITY OF POLYBUTADIENE PREPARED AT 5° C WITH TERTIARY DODECYL MERCAPTAN MODIFICATION

Recipe[a]	Monomer[b]	Phm. modifier[c]	Phm. DIBH[d]	Phm. DETA[e]	Phm. Fe[f]	α/hrs[g]	% modifier in polymer	$\bar{n}_p$	$\bar{n}_n$	$\rho \times 10^4$ [h]
Pers.	Sty.	0.42	—	—	—	0.92/413	0.364	532	530	(1.00)[i]
	Bde.	0.33	—	—	—	0.36/931	0.594	626	663	1.8
j	Bde.	—	—	—	—	—	0.366	1018	1126	1.9
Pyam.	Sty.	0.36	0.16	0.62	0.001	0.43/4	0.164	1182	1085	(0.92)[i]
	Sty.	0.43	0.24	0.60	0.001	0.58/5	0.231	839	777	(0.93)[i]
	Sty.	0.36	0.18	0.20	Nil	0.67/17	0.271	715	700	(0.98)[i]
	Bde.	0.33	0.09	0.09	Nil	0.42/43	0.500	744	811	2.2
	Bde.	0.42	0.17	0.20	Nil	0.33/16	0.492	757	848	2.8
	Bde.	0.35	0.15	0.35	Nil	0.42/18	0.456	817	848	0.9
	Bde.	0.31	0.15	0.19	Nil	0.25/18	0.450	828	922	2.5
	Bde.	0.31	0.15	0.21	Nil	0.52/21	0.344	1084	1255	2.5
	Bde.	0.20	0.18	0.20	Nil	0.36/17	0.305	1223	1440	2.5
	Bde.	0.18	0.18	0.20	Nil	0.46/17	0.245	1523	2051	3.4
	Bde.	0.31	0.09	0.08	Nil	0.45/28	0.213	1752	2513	3.5
	Bde.	0.20	0.16	0.18	Nil	0.40/18	0.242	1542	2512	5.0
Sfx.[k]	Bde.	0.26[k]	—	—	—	0.38/6	0.158	1708	3605	6.2

[a] The kind of recipe described in the experimental section. Pers. indicates persulfate recipe, Pyam. stands for polyamine recipe, and Sfx. represents the sulfoxylate recipe.
[b] Styrene is indicated by Sty. and butadiene by Bde.
[c] Parts tertiary dodecyl mercaptan loaded per hundred of monomer.
[d] Parts diisopropylbenzene hydroperoxide loaded per hundred of monomer.
[e] Parts diethylenetriamine loaded per hundred of monomer.
[f] Parts $FeCl_2 \cdot 6H_2O$ loaded per hundred of monomer.
[g] Fractional conversion of monomer to polymer in the indicated hours of polymerization time.
[h] The terms $\bar{n}_p$, $\bar{n}_n$, and ρ are explained in footnote *g* of Table I.
[i] Styrene results are reported as mole ratio of modifier to polymer.
[j] This was the high molecular weight fraction of polymer immediately above it.
[k] Tertiary octyl mercaptan was used in this experiment.

other termination processes at such low mercaptan levels had caused the real primary chain to be larger than that measured by mercaptan disappearance, or that the loss of low molecular weight material through the osmometer membrane had increased the measured polymer molecular weight.

The data at hand have been examined for the validity of primary chain results but it should be restated that the purification procedures used here caused a loss of less than 3% of the whole polymer. If the polymer lost were devoid of crosslinks, the indicated results would be only about 3% too high.

Results on polymer prepared at 5° C with tetiary alkyl mercaptan are found in Table II. It will be observed that crosslink density results as well as mole ratio in polystyrene are lower with higher initiator levels. This behavior is considered to show that high initiator levels cause mutual termination of two growing chains to take place more frequently and thus reduce the validity of the use of modifier analysis to measure primary chain size. As the initiator

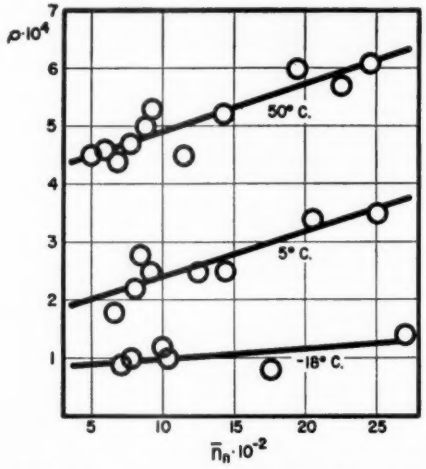


FIG. 2.—The crosslink density, ρ, of polybutadiene prepared at various temperatures with tertiary alkyl mercaptan modification vs. polymer molecular weight, $\bar{n}_n$.

level is reduced, the importance of this error becomes less than the experimental error. It will be noted that at the same molecular weight there is good agreement between results with the persulfate recipe, which should give high crosslink density, and the polyamine, which should give low values if the termination processes are significant. This effect of high initiator levels can also be observed in polymerizations at −18° C in Table III. In both cases, crosslink density does not appear to be a function of conversion, within the range studied, if molecular weights are equal.

It will be noted in Table II that the crosslink density of a high molecular weight fraction of a polybutadiene is not significantly larger than that of the original polymer. This would indicate that crosslinks are uniformly distributed among various size polymer molecules after a few per cent of the lowest fraction has been removed.

TABLE III

CROSSLINK DENSITY OF POLYBUTADIENE PREPARED ON POLYAMINE RECIPE AT −18° C WITH TERTIARY DODECYL MERCAPTAN MODIFICATION

Monomer[a]	Phm. modifier[b]	Phm. DIBH[c]	Phm. TEPA[d]	Phm. Fe[e]	Phm. TSP[f]	α/hrs[g]	% modifier in polymer	$\bar{n}_p$	$\bar{n}_n$	$\rho \times 10^4$[h]
Sty.	0.12	0.20	0.30	Nil	0.45	0.90/19	0.122	1590	1402	(0.88)[i]
	0.15	0.10	0.10	Nil	0.45	0.60/68	0.148	1311	1363	(1.04)[i]
Bde.	0.28	0.18	0.18	0.001	0.45	0.27/20	0.542	686	707	0.9
	0.36	0.27	0.28	0.001	0.30	0.40/43	0.492	757	787	1.0
	0.28	0.18	0.28	0.001	0.30	0.41/42	0.394	946	1003	1.2
	0.40	0.18	0.18	0.001	0.30	0.33/42	0.377	989	1041	1.0
	0.15	0.21	0.28	0.001	0.30	0.26/47	0.200	1867	1663	(—)[j]
	0.12	0.12	0.12	Nil	0.70	0.25/68	0.227	1644	1755	0.8
	0.17	0.21	0.32	0.001	0.30	0.41/20	0.133	2809	2515	(—)[j]
	0.10	0.12	0.12	Nil	0.70	0.30/42	0.165	2263	2699	1.4

[a] Styrene is indicated by Sty. and butadiene by Bde.
[b] Parts tertiary dodecyl mercaptan loaded per hundred of monomer.
[c] Parts diisopropylbenzene hydroperoxide loaded per hundred of monomer.
[d] Parts tetraethylenepentamine loaded per hundred of monomer.
[e] Parts $FeCl_2 \cdot 6H_2O$ loaded per hundred of monomer. Twice this amount of a chelating agent—the tetrasodium salt of ethylenediaminetetraacetic acid—was also loaded.
[f] Parts $Na_3PO_4 \cdot 12H_2O$ loaded per hundred of monomer.
[g] Fractional conversion of monomer to polymer in the indicated hours of polymerization time.
[h] The terms $\bar{n}_p$, $\bar{n}_n$, and ρ are explained in footnote *g* of Table I.
[i] Styrene results are reported as mole ratio of modifier to polymer.
[j] Negative crosslink density indicated by these data.

The high result obtained with the sulfoxylate recipe (Table II) was considered to be due to the low solubility of the monomer in the polymer of the emulsion particle in this recipe, probably due to poor emulsification. Observation of these polymerizations showed a monomer layer persisting beyond 0.52 degree of conversion, a point at which all free monomer should be dissolved in the polymer[9].

In Figure 2, the crosslink density of polybutadiene polymerized at various temperatures is plotted against the polymer molecular weight. The crosslink density decreases with polymerization temperature at a given molecular weight and at low molecular weight of polymers the crosslink density appears to vary linearly with the polymerization temperature. This reduction could be due to any combination of three factors. The type of butadiene addition polymerization, 1,2 vs. 1,4 may be important since the polymer double bonds resulting from the latter may be less susceptible to crosslinking. Some evidence has been presented[12] that the percentage of 1,4 addition polymerization increases with decreasing temperature. The polymer-monomer concentration ratio in the emulsion particle may be reduced at lower polymerization temperature. Since this ratio probably depends on the size of the particle, the kind of continuous phase, and the type of emulsifier as well as temperature, changes made to accomplish polymerization at lower temperatures could also tend to make the ratio smaller. The relative rate of crosslinking to propagation could also be smaller at lower polymerization temperatures.

It will also be noted that crosslink density increases less with polymer molecular weight at −18° C than at the two higher polymerization temperatures, where, as previously suggested, the increase in polymer molecular weight may reduce the polymer-monomer concentration ratio in the emulsion particle. At −18° C the change in the continuous phase, accomplished by the addition

TABLE IV

CROSSLINK DENSITY OF POLYBUTADIENE PREPARED AT 50° C WITH DIISOPROPYL XANTHOGEN DISULFIDE OR PRIMARY DODECYL MERCAPTAN MODIFICATION

Recipe[a]	Monomer[b]	Kind of modifier[c]	Phm. modifier[d]	α/hrs.[e]	% modifier in polymer	$\bar{n}_p$ [f]	$\bar{n}_n$ [f]	$\rho \times 10^4$ [f]
Pers.	Sty.	PDM	0.50	0.93/3	0.303	639	705	(1.10)[g]
	Bde.	PDM	0.75	0.40/11	0.795	467	645	11.8
	Bde.	PDM	0.50	0.31/8	0.648	574	718	7.0
	Bde.	PDM	0.60	0.47/11	0.678	548	754	10.0
	Bde.	PDM	0.50	0.41/12	0.468	796	1159	7.9
	Bde.	PDM	0.30	0.48/11	0.253	1475	2327	5.0
	Sty.	DIX	0.50	0.89/5	0.30	863	892	(1.03)[g]
Hpx.	Sty.	DIX	0.50	0.56/5	0.73	353	378	(1.07)[g]
	Bde.	DIX	0.30	0.30/5.5	0.67	741	938	5.7
	Bde.	DIX	0.20	0.27/3	0.48	1037	1290	3.8
	Bde.	DIX	0.30	0.41/6	0.49	1015	1611	7.3
	Bde.	DIX	0.10	0.27/2.5	0.29	1719	2567	3.8

[a] The kind of recipe described in the experimental section. Persulfate recipe is indicated by Pers. and hydrogen peroxide recipe by Hpx.
[b] Kind of monomer used. Sty. stands for styrene and Bde. for butadiene.
[c] Kind of modifier used. PDM stands for primary dodecyl mercaptan and DIX for diisopropyl xanthogen disulfide.
[d] Parts modifier loaded per hundred of monomer.
[e] Fractional conversion of monomer to polymer in the indicated hours of polymerization time.
[f] The terms $\bar{n}_p$, $\bar{n}_n$, and ρ are explained in footnote *g* of Table I.
[g] Styrene results are reported as mole ratio of modifier to polymer.

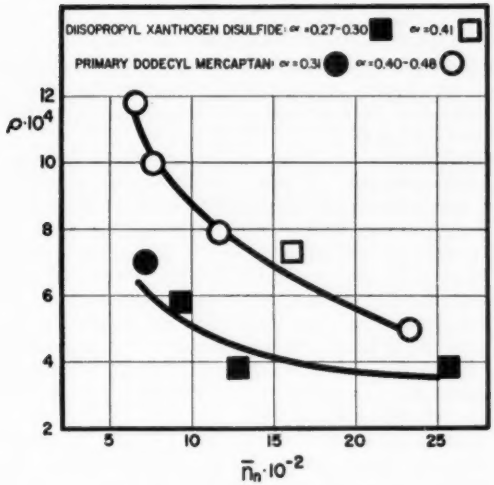


FIG. 3.—The crosslink density, ρ, of polybutadiene prepared at 50° C with either diisopropyl xanthogen disulfide or primary dodecyl mercaptan modification vs. polymer molecular weight, $\bar{n}_n$.

of methanol antifreeze, may cause the polymer molecular weight to have less influence on this concentration ratio.

In Table IV and Figure 3, results from polymers prepared at 50° C with either primary dodecyl mercaptan or diisopropyl xanthogen disulfide modification are shown. Since the calculated crosslink densities decrease with increasing molecular weight and with decreasing conversion, it is considered that these data do not measure actual crosslinking. Primary dodecyl mercaptan is known to add to polymer double bonds[7], and this action would explain the results. There is no evidence that diisopropyl xanthogen disulfide adds to polymer double bonds in a stopped, vented latex, but a more reactive state might be found in a polymerizing system. Any other explanation of results with this modifier would involve the almost complete consumption at 0.30 degree of conversion[13] and the tendency of the recipe used to give low crosslink density results when initiation and termination processes become significant.

CONCLUSIONS

1. A method has been developed for the measurement of crosslink density of diene polymers. This method, which involves the use of radioactive chain transfer agents, is applicable to ungelled polymer prepared under a wide variety of conditions so that any polymerization variable can be studied independently.

2. The crosslink density in polybutadiene decreases with decreasing polymerization temperature. At low molecular weight of polymers, the amount of crosslinking varies linearly with the polymerization temperature.

3. The crosslink density of polybutadiene increases with increasing number-average polymer molecular weight. The rate of increase is less for polymer

prepared at −18° C than for that polymerized at 5° to 50° C. This means that, in a polymerization, as the average molecular weight increases with conversion the crosslink density increases. However, when the molecular weight is kept constant, by changes in the modifier loading, the crosslink density of polybutadiene appears to be independent of the degree of conversion attained within the range of 0.12–0.48.

4. The crosslink density of a high molecular weight fraction of polybutadiene was not significantly different from that of the whole polymer (from which about 3% of low molecular weight material had been removed).

5. The kind of initiator system does not affect the crosslink density of polybutadiene, providing the initiator loading is not too high. However, if large amounts of initiator are used in the polymerization, 10% or more of the polymer molecules may not contain mercaptan modifier.

6. Tertiary alkyl mercaptans are necessary for the crosslinking studies because they do not appear to give side reactions. Primary dodecylmercaptan and diisopropyl xanthogen disulfide are unsatisfactory for determinations because they appear to add to the double bonds of the polymer molecule in addition to the usual chain transfer reactions.

7. Incomplete emulsification of monomers in some 5° C recipes apparently increased the crosslink density of polybutadiene by retarding the diffusion of monomer into the monomer-polymer particles.

SYNOPSIS

The crosslink density in polybutadiene has been determined by measurement of the polymer molecular weight by osmometry and the primary chain molecular weight by modifier analysis involving radioactive materials. Since the number of polymer molecules is equal to the number of primary chains less the number of crosslinkages, the experimental measurements may be used to calculate the crosslink density. This method can be used to determine crosslink density at a combination of conversions, modifier loadings, and polymerization temperatures which could not be done by other methods. Branching and cyclic structure forming crosslinks are not measured by this method, the principal assumption of which is that one and only one modifier fragment is attached to each primary chain. Initiation and termination processes tend to reduce the validity of this assumption, but these have been minimized by rereduction of the amounts of initiator and found insignificant by comparison of different systems. Modifiers which react with polymer in nonterminal positions also reduce the validity so that primary dodecyl mercaptan was not satisfactory as a modifier in this work, while tertiary alkyl mercaptans were. Also, diisopropyl xanthogen disulfide was not satisfactory because of secondary reactions. The crosslink density of polybutadiene prepared in emulsion decreases with decreasing polymerization temperature. At a given molecular weight, the crosslink density does not appear to be a function of conversion within the range studied. At a given polymerization temperature, increasing polymer number average molecular weight was accompanied by increasing crosslink density although the rate of such increase was smaller at subfreezing polymerization temperatures. These results agree with kinetic theory of crosslinking in emulsion polymerization, but actual values are higher than those obtained in comparable systems by the gel point method.

REFERENCES

[1] Morton, M., and Salatiello, P. P., *J. Polymer Sci.* **5**, 225 (1951).
[2] Morton, M., Cala, J. A., and Piirma, I., *ibid.* **15**, 167 (1955).
[3] Drysdale, J. J., and Marvel, C. S., *ibid.* **13**, 513 (1954).
[4] Stockmayer, W. H., *J. Chem. Phys.* **12**, 125 (1944).
[5] Sands, G. D., and Johnson, B. L., *Ind. Eng. Chem., Anal. Ed.* **19**, 261 (1947).
[6] Smith, W. V., and Ewart, R. H., *J. Chem. Phys.* **16**, 592 (1948).
[7] Kolthoff, I. M., and Harris, W. E., *J. Polymer Sci.* **2**, 49 (1947).
[8] Flory, P. J., *J. Am. Chem. Soc.* **69**, 2893 (1947).
[9] Meehan, E. J., *ibid.*, **71**, 628 (1949).
[10] Kolthoff, I. M., Meehan, E. J., and Medalia, A. I., private communication to Reconstruction Finance Corporation, Office of Rubber Reserve, Progress Report, January 1949, University of Minnesota, CR-2007, pp. 100–122.
[11] Bardwell, J., and Winkler, C. A., *Can. J. Research* **B27**, 116 (1949).
[12] Hart, E. J., and Meyer, A. W., *J. Am. Chem. Soc.* **71**, 1980 (1949).
[13] May, D. R., and Kolthoff, I. M., *J. Polymer Sci.* **4**, 735 (1949).

CIS TO *TRANS* ISOMERIZATION OF POLYISOPRENE *

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Although polybutadiene readily undergoes photochemical[1] or radiation chemical[2] *cis* to *trans* isomerization in solution sensitized by bromine atoms or thiyl radicals, no such isomerization has been achieved with polyisoprene. Moreover, although polyisoprene has been isomerized to a variety of resins[3], no evidence for any *cis* to *trans* change in this polymer has been heretofore described. This communication reports the *cis* to *trans* isomerization of polyisoprene in solution catalyzed by elemental selenium at temperatures of around 180–200° C. A common structure was obtained having a *cis/trans* ratio estimated to lie somewhere between 50/50 and 60/40, starting with either the essentially all-*cis* polyisoprene (Hevea) or all-*trans* polyisoprene (balata). The mechanism presumably involves π complexing of the polymer double bonds with selenium in the manner depicted for the selenium-catalyzed isomerization of oleic acid[4] and stilbene[5].

A 2–3% solution of Hevea or balata in a suitable high-boiling solvent such as *o*-dichlorobenzene or tetralin, containing 0.5 g/l powdered selenium, was refluxed under nitrogen for 2–5 hours. Subsequently the solution was cooled, and filtered to remove the selenium which separated out. Methanol was added to the filtered solution to coagulate the polymer, which was washed with alcohol, airdried and its structure analyzed by infrared absorption procedures. The recovered polymers were lower in molecular weight than originally, dropping in a typical case (e.g., Hevea) from a viscosity average molecular weight of about 550,000 to 300,000.

The infrared spectrum of the polymer obtained on treatment of *either* Hevea or balata with selenium is shown in Figure 1, together with the spectra of the starting polymers. The spectrum of amorphous balata is shown, instead of that of the crystalline polymer, since isomerization of some of the *trans* units in balata into *cis* units destroys its normal crystallinity. Otherwise, the spectrum of an isomerized balata would show greater change than could be ascribed just to the *trans* to *cis* conversion. The absorption bands which should be compared are indicated by arrows. The spectra show that the two kinds of polyisoprene, treated in the manner described above, were indeed isomerized to a common structure intermediate between the initial all-*cis* and all-*trans* structures. Thus, the bands in spectrum B at 8.80, 9.18, 9.67 and 11.92 μ all occur at wave lengths which are in between those of the corresponding bands in spectra A and C (8.88 and 8.70 μ; 9.25 and 9.10 μ; 9.65 and 9.70 μ; 11.94 and 11.86 μ, respectively). Also, the strong band in B at around 12.0 μ, which is due to absorption by both *cis*-1,4 and *trans*-1,4 units in polyisoprene, has a broadness which is intermediate between that in A and that in C. A very

* Reprinted from the *Journal of Polymer Science*, Vol. 36, pages 523 (1959).

interesting feature of B is the appearance of the two peaks at 7.65 and 7.55 μ which evidently arise from the 7.68 μ band in Hevea and the 7.52 μ band in balata, respectively. That they can be assigned unambiguously to *cis* and *trans* units was confirmed by examination of the spectra of various synthetic mixtures of Hevea and balata, all of which showed these two peaks but with different intensities depending upon the relative proportions of the *cis* and *trans* polymers present in the mixtures.

Some uncertainty was encountered in estimating the equilibrium *cis* to *trans* ratio of the isomerizate by means of infrared absorption. By comparing spectrum B with the spectra of the synthetic mixtures and matching the two which looked most alike in the 7.5–7.7 μ region, a value of about 50/50 was obtained for the *cis* to *trans* ratio. On the other hand, comparing the 8.80 μ region in B with the corresponding regions in the spectra of the various syn-

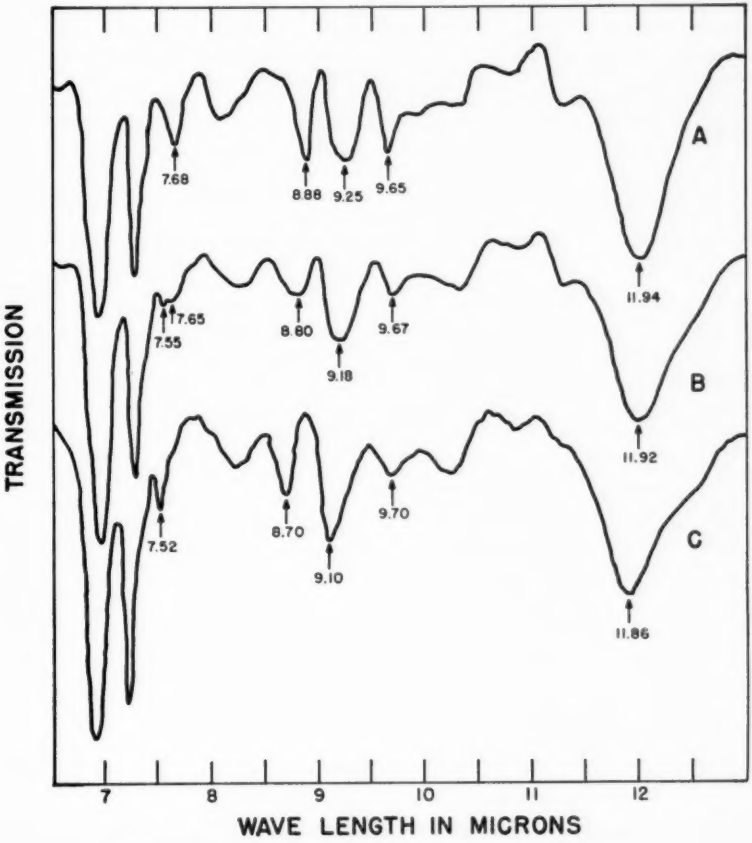


FIG. 1.—The infrared spectrum of isomerized polyisoprene (B) compared with the spectra of Hevea (A) and amorphous balata (C).

thetic mixtures gave instead a value of about 60/40 for this ratio. No definite explanation for this anomaly is available at present, but it may be that isolated *cis* and *trans* double bonds do not have the same absorptivities at the various wave lengths as they do in the pure *cis* or pure *trans* polymers. Further work is planned in order to resolve this anomaly. Because of these difficulties with the 7.5–7.7 μ and 8.7–8.9 μ regions of the polyisoprene spectrum, no attempt was made to calculate a *cis* to *trans* ratio for the isomerizate using the method of Binder and Ransaw[6]. Instead, we can only assume at this time that the equilibrium ratio must lie somewhere in the range indicated above.

A *cis* to *trans* isomerization of polybutadiene in solution also was accomplished with selenium as catalyst, resulting in an equilibrium *cis* to *trans* ratio for this polymer of 15/85 at about 200° C.

The assistance of J. J. Shipman with the infrared analysis is gratefully acknowledged.

REFERENCES

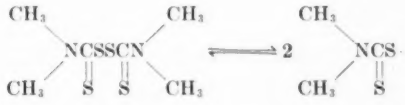
[1] Golub, M. A., *J. Polymer Sci.* **25**, 373 (1957); RUBBER CHEM. & TECHNOL. **30**, 1142 (1957).
[2] Golub, M. A., *J. Am. Chem. Soc.* **80**, 1794 (1958); *ibid.* **81**, 54 (1959).
[3] Whitby, G. S., Ed., "Synthetic Rubber", John Wiley & Sons, Inc., New York, **1954**, p. 614–7
[4] Fitzpatrick, J. D. and Orchin, M., *J. Am. Chem. Soc.* **79**, 4765 (1957).
[5] Fitzpatrick, J. D. and Orchin, M., *J. Org. Chem.* **22**, 1177 (1957).
[6] Binder, J. L. and Ransaw, H. C., *Anal. Chem.* **29**, 503 (1957).

VULCANIZATION WITH TMTD *

E. M. Bevilacqua

In the presence of a slight excess of zinc oxide, bis(dimethylthiocarbamoyl) disulfide (tetramethylthiuram disulfide, TMTD[1]) reacts with rubber[2–4] and with some other olefins[5] to form a high yield of crosslinks. Certain features of this reaction have made it attractive as a starting point in the study of the mechanism of vulcanization with sulfur. The combination of TMTD and zinc oxide appears to be much less complex than the mixtures required to obtain efficient crosslinking[6] when sulfur is the primary vulcanizing agent. The crosslink yield is as high as can be obtained by any known method which produces crosslinks involving sulfur[6–8]. Per mole of sulfur combined with the hydrocarbon, the yield is the same as that obtained by vulcanization with the most efficient known combination of sulfur, accelerator, and zinc soap under conditions which maximize the yield[8]. A large fraction of the TMTD taken can be accounted for as a single well defined compound after completion of the vulcanization reaction[9,10]. The combination of simplicity and high yield of known products suggests that there may be found a stoichiometric reaction which will account for vulcanization with TMTD, in contrast to the apparently complex mixture of reactions which occur in vulcanization with sulfur.

Several reaction mechanisms which involve the concept of a possible stoichiometric reaction have been discussed in the literature, some more fully worked out than others. The earliest speculations on the mechanism have been reviewed recently by Craig and coworkers[11] and by Scheele and coworkers[10]. The first interpretation[12,13] considered the efficiency of TMTD to be related to the formation of the effective accelerator ZnDMDC (zinc dimethyldithiocarbamate), which is formed in high yield by reaction of TMTD and zinc oxide at elevated temperatures. Later mechanisms have for the most part involved interaction of the TMTD with the hydrocarbon prior to formation of the dithiocarbamate. A relatively straight forward possible mechanism was first discussed by Farmer[14], who pointed out the analogy between the structure of TMTD and the symmetrical peroxides:

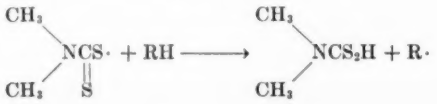


(1)

Since Farmer's first discussion it has been well established that some peroxides will vulcanize rubber by removing hydrogen atoms to form hydrocarbon radicals which vanish substantially exclusively by combination[15], forming carbon-to-carbon crosslinks. If thiocarbamate radicals are equally efficient then vulca-

* An original contribution.

nization could occur in an exactly analogous manner:



$$2R\cdot \longrightarrow RR \qquad (3)$$

A number of other reaction schemes, progressively more elaborate, but all involving dissociation of TMTD with subsequent attack on the hydrocarbon have been discussed by Bergem[16], by Craig and coworkers[17–19], by Jarrijon[9], and by Bielstein and Scheele[20]. The recent discussion by the last workers is perhaps the most detailed and suggests obvious experimental tests for the mechanism outlined. By logical extension of each of the other mechanisms discussed, certain simple experimental tests can be devised, some of which have already been made and described. These are treated as follows under the headings Tests 1 to 4.

TEST 1

If vulcanization with TMTD in the presence of zinc involves only formation of dithiocarbamate and sulfur which then vulcanize the rubber in the same way as a simple mixture of these two compounds, it should be possible to obtain the

TABLE I

COMPARISON OF VULCANIZATION EFFICIENCIES

A. Formulas:		
Pale crepe	100	100
Zinc oxide	5.0	2.5
ZnDMDC	—	6.4
TMTD	7.5	—
Sulfur	—	1.0
200% stress	225	75
Sulfur combined %	0.50	0.69
"Sulfide" sulfur	0.04	0.20
Theory: sulfur combined	0.54	—
Cure: 24 Hours @ 108° C		
B. Formula:		
Pale crepe	100	
Zinc oxide	5	
TMTM	6.5	
Sulfur	1.0	
Cure cycle (see text):	*1*	*2*
Sulfur withheld	No	Yes
200% stress	230	100
Sulfur combined %	0.56	0.78
Theory	0.54	—
ZnDMDC formed	6.38	5.37
Theory	5.65	—
"Sulfide" sulfur	0.04	0.10

same efficiency of vulcanization without starting with TMTD. Since the yield of dithiocarbamate during vulcanization is now known[10], the simple comparison of TMTD and accelerated vulcanization in Table IA can be made. Two compounds were prepared, one being a mixture of pale crepe, TMTD and enough zinc oxide for maximum utilization of the TMTD. The other compound contained sulfur equivalent to the TMTD, together with ZnDMDC approximately equal to that formed during vulcanization with TMTD and zinc oxide to keep the total zinc concentration about the same. These were each cured in a platen press for the same length of time. Three differences between the vulcanizates can be seen. The stress at low strain is higher for the TMTD compound, the combined[4] sulfur is lower, and the sulfur appearing as sulfide on analysis is lower. These differences would be anticipated. Under mild conditions in a compound containing free sulfur, sulfide sulfur is formed during the oxidation of a rubber-sulfur intermediate by the molecular sulfur[6,7]. In the TMTD vulcanizate excess TMTD serves this purpose (cf. below).

Similar evidence is afforded by Part B of Table I. For this experiment an equivalent mixture of TMTM and sulfur was used instead of TMTD. For cure cycle *1* of the table, the compound was mixed as given and cured twenty-four hours at 108° C. For cycle *2* the sulfur was omitted in the first mixture

TABLE II

COMPARISON OF TMTD AND SULFUR VULCANIZATES[a]

Cure temperature[a]	200% stress[b]	
	TMTD	Sulfur
100	300	300
120	300	265
140	297	223
160	290	172

[a] All samples were heated in a press at the indicated temperature until modulus stopped rising.
[b] Compounds were chosen to give as high a modulus per mole of combined sulfur as possible[6].

which was heated under curing conditions twenty-four hours. No cure resulted. Sulfur was then added and an additional cure of one day at 108° given. Here again the complete system is much more efficient in producing crosslinks than one containing ZnDMDC and sulfur.

Another piece of evidence arguing against simple reaction of TMTD with zinc oxide followed by an independent vulcanization exists in the observation by Barton that the yield of crosslinks as measured by modulus is substantially independent of the temperature of cure with this compound, in contrast to accelerated sulfur vulcanization, for which the crosslink yield is very sensitive to temperature (Table II).

TEST 2

If pure carbon-to-carbon crosslinking results from the reaction with TMTD, it should be possible to obtain vulcanizates containing no sulfur by appropriate treatment of the rubber after completion of the reaction. Although no investigation having this specific objective has been reported, the results of a number of workers strongly imply that sulfur does remain attached to the hydrocarbon after vulcanization[4,5,21]. If the mechanisms outlined in Equations (2) and (3) were operative, a substantially quantitative yield of dithiocarbamate would be expected. The extensive studies by Scheele and coworkers leave little doubt

that the yield is not quantitative in the sense of these equations, but approximately four equivalents of dithiocarbamate are formed per three moles of TMTD[10].

TEST 3

The considerations in the previous paragraph do not apply if carbon-to-carbon crosslinks were to be formed by some process in which addition of fragments of the vulcanizing agent to the double bond of the hydrocarbon or attachement in other ways were combined with the formation of carbon-to-carbon crosslinks. However, if fragments are attached in a reaction which is stoichiometric then: (a) the nitrogen/sulfur ratio after removal of all soluble material should be constant and directly related to the TMTD taken; (b) since the sulfur would appear as thioamide, it would be expected to be hydrolyzed by acid to form hydrogen sulfide; (c) the amine fragment might also be expected to be susceptible to hydrolysis and detection as free amine. Finally, if any carbon-to-carbon bonds are formed, it should be difficult to render the vulcanizate soluble by means of simple reducing agents.

It has been repeatedly observed that some nitrogen[3,5,22,23] is found in products of the reaction of TMTD with hydrocarbons, implying that fragments are

Table III

Nitrogen in Fully Cured Vulcanizates

TMTD taken (g/100 g rubber)	Nitrogen[a] (wt. % found)	Nitrogen[b] (wt. % calc.)
2	0.37	—
4	0.37	0.45
6	0.34	0.53
8	0.38	0.61
10	0.40	0.63
12	0.43	0.69
15	0.55	0.77

[a] Analyses of samples extracted continuously four days at room temperature with chloroform.
[b] Calculated as excess over first sample, if reaction occurred according to Bielstein and Scheele[10].

indeed attached to the carbon chain. However, the amount found does not appear to be sufficient to be consistent with effectively quantitative addition of the vulcanizing agent to the hydrocarbon. It is known that TMTD vulcanizates can be obtained in which substantially no sulfur is present in a form which is released as hydrogen sulfide upon digestion with strong acid. The formation of "sulfide" sulfur appears to be the result of inefficient use of the TMTD for crosslinking during vulcanization, resulting from competitive reactions which become important at higher temperatures. The problem of sorting out reactions and products essential to the vulcanization becomes more critical as the temperature is raised, because the reaction mixture is heterogeneous and diffusion control can exert a major influence on the results observed. An additional complication exists in the apparent possibility for TMTD to disappear by both radical and polar reactions, the latter becoming important at just the temperatures conventionally used for vulcanization.

Among the mechanisms involving addition of fragments to the hydrocarbon, that of Bielstein and Scheele is presented in such a way as to permit exact quantitative testing. According to the mechanism as outlined, two atoms of nitrogen and four of sulfur would remain attached to the hydrocarbon after

vulcanization. Tables III and IV contain estimates of total nitrogen and of "dimethylamide" in fully cured vulcanizates after prolonged (96 hour) continuous extraction with cold chloroform.

The efficiency of extraction by this procedure has been tested by analyzing fully extracted samples for dithiocarbamate[4], which is difficult to remove. The nitrogen values reported in Table III represent an upper limit to the amount which could be present directly attached to the hydrocarbon and include any remaining as a result of incomplete extraction.

As discussed above, half the sulfur should be observed as "sulfide" sulfur upon digestion with strong acid, but under mild conditions little or none is formed.

Bateman and coworkers[24] have reviewed the evidence pertaining to solubilization of sulfur containing vulcanizates by reducing agents. They do not specfically discuss the most efficient vulcanizing combinations, but it has been found that a TMTD vulcanizate will dissolve in mercaptoacetic acid.

TABLE IV

"DIMETHYLAMIDE" IN TMTD VULCANIZATES

"DMA" found[a] (moles/10^4 g)	"DMA" calculated[b] (moles/10^4 g)
0.11	0.83
0.18	1.40
0.21	3.07
0.35	3.35
0.38	4.20

[a] Values given are total volatile base found on titration with standard acid after digestion of the extracted vulcanizate alternately with dilute phosphoric acid and with 2*N* sodium hydroxide in ethanol. The conditions may not be sufficiently vigorous to conclude on this evidence alone that dimethyl amides are not formed.

[b] According to Bielstein and Scheele[30].

TEST 4

If crosslinking involves a reaction in which hydrogen atoms are removed from the hydrocarbon, they should appear as some final product in the vulcanizate. If the predominant reaction involves addition at a double bond, unsaturation of the polymer should decrease in proportion to the extent of crosslinking. It is difficult to measure unsaturation with the accuracy required to resolve the problem on this basis[25] but efforts which have been made suggest that efficient crosslinking is not accompanied by quantitative loss of unsaturation. Analysis of reaction products of low molecular weight olefins with TMTD suggest some saturation of double bonds[24,26,27] but it is not entirely clear how far this applies to rubber. For small changes in unsaturation the alternative test, removal of hydrogen atoms, may be a more sensitive measurement of the relative importance of substitution and addition reactions. It has been observed repeatedly that decomposition products of dimethyldithiocarbamic acid are formed during reaction of polyisoprenes[21,23,28] with TMTD, implying that hydrogen atoms are removed from the hydrocarbon. French[23] has observed that free lauric acid may be isolated from the reaction of TMTD, rubber and pure zinc laurate. It is particularly pertinent that Bloomfield[5] observed the formation of H_2S from the reaction of TMTD and rubber.

In the presence of sufficient zinc oxide to yield the maximum possible number of crosslinks, it would be anticipated that the protons would appear as

water. The results of an experiment to determine the ratio between TMTD taken and water formed are summarized in Figure 1.

For this experiment squalene, TMTD, and zinc oxide were heated in sealed tubes 48–72 hours @ 98° and water determined by titration with Karl Fischer reagent. The high zinc oxide blank on direct titration was unsatisfactory, so later samples were prepared by distillation of the water from the reaction mixture diluted with toluene and titration of the water-toluene mixture. Results of both sets of experiments are shown in Figure 1.

In addition to the evidence in the preceding paragraphs (Tests 1–4) any mechanism must account for certain other observations. Bloomfield[5] has

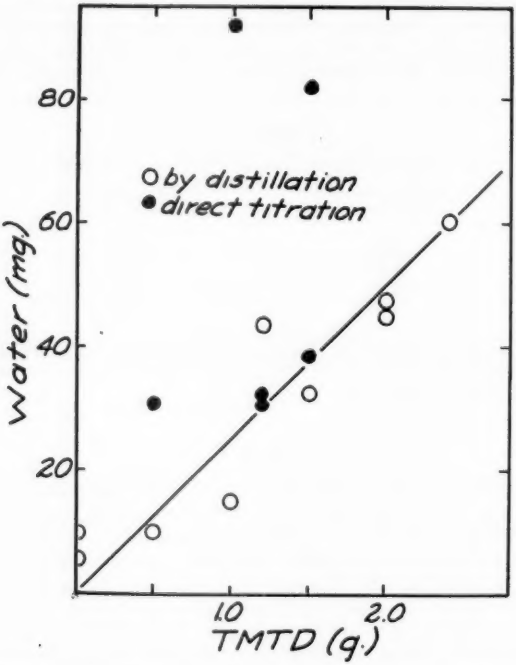


FIG. 1.—Water formed during reaction of TMTD and squalene in the presence of excess zinc oxide. Squalene taken was either five or ten grams. The line has theoretical slope.

reported that TMTD reacts with rubber much faster than it decomposes alone at the same temperature. Lorenz, Scheele, and Redetsky[29] have shown that there appears to be a close relationship between formation of crosslinks and formation of dithiocarbamate. Crosslink formation depends on rubber soluble zinc being present; TMTD decomposition does not.

In 1952 Moore[30] described experiments on the reaction of 2,2′-bis(benzothiazolyl) disulfide, MBTS, with olefins. His results were interpreted in terms of a chain reaction involving MBT radicals. The obvious analogy to TMTD suggested that the reaction of these two materials might prove to be similar,

although complicated by the greater thermal instability of the latter compound. A preliminary report of a mechanism based on this observation has been published[31]. It appears to account for all of the evidence which has been discussed thus far. In the subsequent discussion other evidence bearing on the mechanism will be reviewed.

EXPERIMENTAL

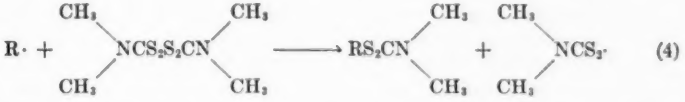
All rubber compounds were mixed by conventional techniques on two-roll laboratory rubber mills and cured in platen presses with temperature adjusted by steam pressure supplied to the platens. Rubber chemicals were principally commercial materials: Blended No. 1 pale crepe, Tuex (commercial TMTD, U. S. Rubber Company) used as received, except for the experiment of Figure 1 for which it was repeatedly crystallized from chloroform and alcohol and dried in vacuo, Kadox (a fine particle zinc oxide, New Jersey Zinc Company), Methazate (ZnDMDC, U. S. Rubber Company), Laurex (commercial zinc laurate, U. S. Rubber Company). MBTS was prepared for one experiment by oxidation of purified "mercaptobenzothiazole" with iodine in aqueous alkali. Squalene was used as purchased from Distillation Products Industries.

Stress-strain properties were measured with an autographic instrument using ring test pieces, in use in the laboratories of the U. S. Rubber Research Center. Results are reported in pounds per square inch of unstrained cross section on first extension at a relative length of three (200% stress) or two (100% stress).

Other analyses involve conventional analytical methods. Modifications are indicated in the discussion. Sulfur not removed from the vulcanizate by successive treatment with a mixture of acetic and hydrochloric acids at reflux and extraction with butanone is reported as "combined" sulfur. Sulfur released as hydrogen sulfide by the acid treatment is called "sulfide" sulfur.

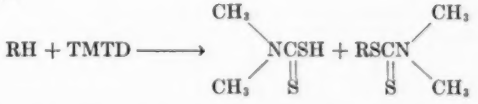
DISCUSSION

The published mechanism includes three distinct stages of which only the first may involve radical reactions. In the first stage rubber reacts by a long radical chain process to give a polyisoprene dithiourethan (dithiocarbamate). Initiation may be by Reaction (1), the chain carrying steps, (2) and (4).



(4)

If the chain is sufficiently long the overall stoichiometry is the sum of Equations (2) and (4)

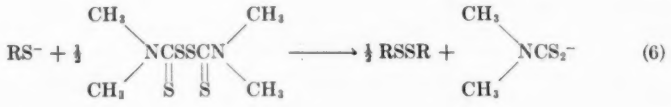


(5)

The dithiocarbamic acid reacts rapidly with zinc oxide (or zinc soap).

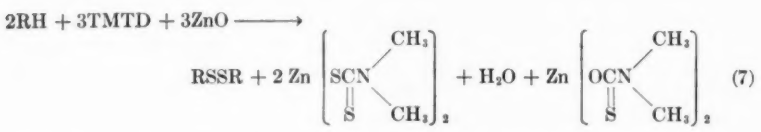
In the second stage the dithiourethan is hydrolyzed by a rubber soluble zinc salt. Normally in rubber there is a sufficient quantity of fatty acid naturally

present or added during mixing to dissolve some zinc oxide. Products of the hydrolysis of the dithiourethan were predicted to be a mercaptide and a thionocarbamate. Finally, the mercaptide is oxidized by TMTD to a disulfide:



(6)

Overall the reaction is:



(7)

Each of these equations is considered separately in the discussion following.

EQUATION (1)—DISSOCIATION OF THE DISULFIDE

The reaction represented by Equation (1) provides a source of radicals to initiate the chain carrying steps (2) and (4). It is not essential to the mechanism, since alternate ways for initiation to occur are available. Zinc oxide reacts[32,33] with TMTD in the absence of rubber to yield ZnDMDC. There is some direct evidence that this reaction occurs as a side reaction at appreciable rates at temperatures at which vulcanization occurs when not enough zinc is in solution in the rubber. It has been found that the amount of dithiocarbamate formed retains the ratio to TMTD taken of four thirds (equivalents/mole) under conditions where the maximum possible yield of crosslinks was not obtained[4]. The zinc salt is an active accelerator of sulfur vulcanization. A trace of this, once formed, might then initiate the chain carrying reactions. However, although this may be an auxiliary source of initiation once vulcanization starts, it is not considered likely to be the principal one. Addition of dithiocarbamate to a TMTD-zinc oxide-rubber mixture does not accelerate increase in modulus appreciably. TMTD dissolved in rubber disappears at approximately the same rate whether zinc is present or absent. More directly to the point, Ferington and Tobolsky[34a,b] have investigated the activity of TMTD as a polymerization catalyst[35] and found that it approaches benzoyl peroxide in activity. This indicates dissociation into radicals which attack the hydrocarbon at temperatures at which vulcanization occurs, rapidly enough to be the sole source of initiation.

Dissociation at the central S—S bond rather than at a C—S bond is based partly on analogy with MBTS, partly on the structure of products of the reaction (cf. below). Simple aliphatic disulfides have bond strengths of the order of — 70 kcal per mole in the central S—S bond as well as in the C—S bond[36]. This is much too high for appreciable thermal dissociation into radicals at moderate temperatures to take place. But in thiuram disulfides potential resonance stabilization of the radicals resulting should appreciably

weaken the central bond. The related compound MBTS dissociates to a measurable extent in solution and from the change in equilibrium[37]

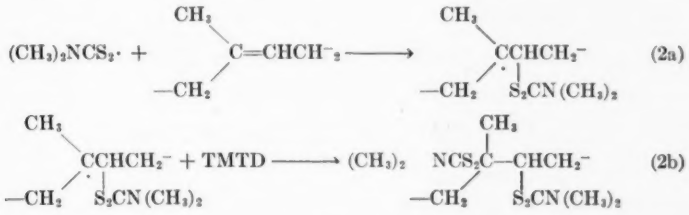
$$ArSSAr \rightleftharpoons 2ArS\cdot$$

with temperature a value of D ~ 29 kcal per mole has been calculated[38]. No corresponding measurements have been reported for TMTD as yet.

Solutions of TMTD in solvents with which it does not react have been observed to undergo a qualitatively reversible color change on heating and cooling; it was also reported that Beer's Law is not obeyed by TMTD solutions at room temperature[16]. These effects have been attributed to reversible dissociation into (long-lived) radicals. The thermochromism has not been studied quantitatively and is not unequivocal evidence for dissociation into symmetrical radicals. Although MBTS dissociates, the color changes which it undergoes in solution on heating have been attributed to another cause[40]. The apparent failure of TMTD to obey Beer's Law in solution has been associated with rapid irreversible changes in solutions[40], presumably resulting from the well-known sensitivity of this compound to light[34,35].

EQUATION (2)—REACTION OF THIOCARBAMOYL RADICALS WITH RUBBER HYDROCARBON

Reactions (2) and (4) together constitute the chain carrying steps which give a high yield of product per initiating radical. There is not unequivocal evidence on which to assess the relative probability of Reaction (2) and the alternative (2a) which may be written:



(2a)

(2b)

but several considerations suggest that (2) and (4) should be preferred in the absence of more direct evidence. In spite of repeated efforts it has not proved possible to obtain addition of simple sulfur radicals at double bonds of rubber, even though this occurs with low molecular weight hydrocarbons[42]. Where the occurrence of rubber-S_2 radicals is a plausible expectation (resulting from α-methylene attack) these form S_4 crosslinks by combination[27]. Ability to add to the double bonds of rubber has been shown to be related to the acid dissociation constant[42] of the corresponding sulfhydryl compound. The dissociation constant for dimethyl dithiocarbamic acid has not been estimated, but it should be much less dissociated than the thiol acids which are known to add.

It is necessary to account for the high yield of dithiocarbamate obtained during the vulcanization reaction. If double bond addition occurs according to (2a) and (2b) then the elements of dithiocarbamic acid must be lost from this combination quantitatively to give the same stoichiometry as Equation (5) at

some subsequent stage in order to make this accounting. On steric grounds it would be anticipated that the residue attached to the tertiary carbon atom would split out preferentially. If so, a trisubstituted ethylenic group would result, without extensive double bond shifting along the chain. Experimentally, it is known that some shift does occur. Evidence for this was originally found in studies of the effect of vulcanization on the infrared spectrum of rubber[43]. During vulcanization with sulfur a new absorption band appears at 10.4 μ, which is rendered more intense by additions which would be expected to increase the efficiency of crosslinking. This band has been assigned to structures of the form *trans*-RCH=CHR, which can be formed in rubber only by a double bond shift along the chain, away from the tertiary carbon atom.

The infrared absorption at 10.4 μ is unfortunately difficult to assay quantitatively at the concentrations occurring in vulcanization. The assignment to *trans* double bonds has been questioned[24], but the fact that every change which would be expected to increase efficiency of crosslinking increases the intensity of the band and the evidence cited in the next paragraph both weigh against the alternate assignment exclusively to cyclic structures. A band appears at the appropriate location in the spectrum of rubber vulcanized with cumyl peroxide. Assuming the same extinction coefficient as that occurring in *trans* polybutadiene, in the absence of a closer model, the yield of *trans*-RCH=CHR is consistent with the interpretation given here. It is 10–15% (moles/mole) of the amount of peroxide taken, when vulcanization is carried out at a nominal temperature of 150°.

Independent evidence from the investigation of the interaction of rubber with molecular oxygen led to the conclusion that this double bond shift occurs and its extent is temperature dependent; at temperatures at which vulcanization is frequently carried out, the shift may be substantially complete[44] in the sense of Equation (8)



(a) (b) (8)

This complementary evidence from two distinct experimental methods implies that both oxidation and vulcanization are free radical reactions, involving at one stage a common intermediate. An allylic intermediate like (8a) or (8b) will occur in Reactions (2) and (3) but is not expected in (2a) and (3a).

In passing it may be noted here that this interpretation would explain why sulfur inhibits oxidation and oxygen inhibits vulcanization.

REACTION (4)—ATTACK ON TMTD BY HYDROCARBON RADICAL

Reaction (4) produces the first important "stable" intermediate. Ferington and Tobolsky[34] have shown that TMTD is a moderately efficient retarder in vinyl polymerization; it must, therefore, be readily attacked by hydrocarbon radicals. There is no published evidence to show directly that this reaction involves symmetrical scission of the molecule, but the same considerations applying to dissociation into radicals may be presumed to apply in the transfer reaction. Ferington and Tobolsky have concluded that unsymmetrical scission of TMTD must be involved in the retardation of vinyl polymerization and symmetrical scission in thermal initiation, principally on the basis of a compari-

son of the behavior of TMTD and TMTM. An alternative explanation appears to be available:

Retardation is the result of attack by a hydrocarbon radical on the vulcanizing agent and is not necessarily dependent on ability of the compound to dissociate of itself into radicals. The attack is presumably on sulfur rather than on carbon. Reaction (4) may then be taken to represent retardation by TMTD. TMTM would form a different radical in the same process.

$$(CH_3)_2NCSSCSN(CH_3)_2 + R\cdot \longrightarrow RS_2CN(CH_3)_2 + (CH_3)_2NCS\cdot \qquad (4a)$$

TMTD then retards and TMTM does not because $(CH_3)NCS_2\cdot$ is less active in initiating a new polymer chain than $(CH_3)NCS\cdot$. This interpretation should be subject to a simple test by appropriate sulfur analyses on the polymer.

When azo-bis isobutyronitrile and TMTD are heated together in solution in benzene for several half lives of the nitrile, a high yield of a new compound $C_7H_{12}N_2S_2$ is formed. While it has not been fully characterized, this compound has the composition expected on the basis of Reaction (4); it is not a molecular compound of TMTD and tetramethylsuccinonitrile.

$$\begin{array}{l} CH_3 \\ | \\ NCC\cdot \\ | \\ CH_3 \end{array} + \tfrac{1}{2}\,\text{TMTD} \longrightarrow \begin{array}{l} CH_3 \\ | \\ NCCS_2CN(CH_3)_2 \\ | \\ CH_3 \end{array} \qquad (4b)$$

SECOND STAGE: "HYDROLYSIS" OF THE INTERMEDIATE

French[23] observed that alkyl esters of dimethyldithiocarbamic acid react with alcoholic sodium hydroxide to give mercaptans. There appears to be no evidence available in the literature on the hydrolysis of dithiourethans although related compounds have been examined[45]. An excess of zinc oxide over that required by the stoichiometry of the reaction must be present for full development of modulus, indirectly indicating that a simple alkaline hydrolysis step occurs. An early experiment clearly indicating that a stoichiometric relation exists between zinc oxide taken and crosslink yield was made by Barton[8], who compared stress at low strain for varied zinc oxide levels at one TMTD level. It is difficult to make this determination from measurements of stress at high strain[40] because the contribution from crystallization[2] obscures differences due to crosslink density changes. Barton's observations have been extended, with results summarized in Figures 2 and 3. These show: (a) there appears to be a definite minimum amount of zinc oxide required for full development of modulus (i.e., of crosslinking) from a given amount of TMTD, the modulus being approximately a linear function of zinc oxide below this concentration, (b) this minimum is a linear function of TMTD, corresponding to slightly more than one mole per mole, and (c) it is free base which is required, not just zinc in a soluble form. The explanation for this follows obviously from the observations of Craig, Juve, and Davidson[47] on the reaction of acids with TMTD and the evidence discussed in connection with Figure 1.

It is possible to show that the reaction of rubber and TMTD leads to an intermediate containing about twice as much total sulfur combined with the hydrocarbon as sulfur remaining after hydrolysis, although it has not yet been established that this intermediate will react with zinc oxide and an oxidizing agent to yield crosslinks. It has also been found that mercaptan groups can

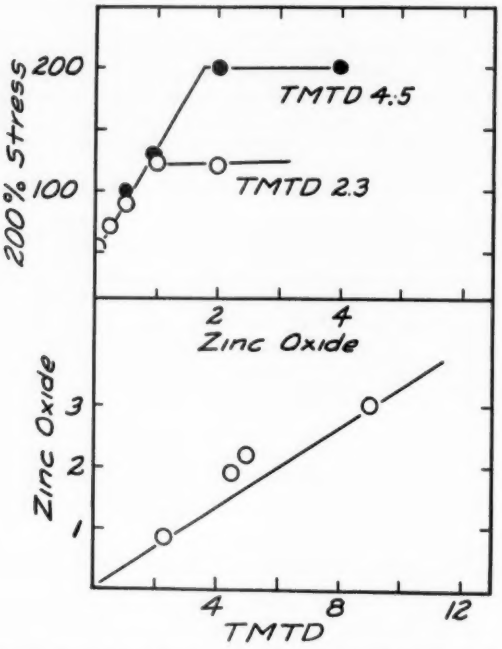


FIG. 2a (above).—Modulus of pale crepe-TMTD-zinc oxide vulcanizates at two TMTD levels as a function of zinc oxide level. Specimens cured 24 hours @ 108°. Units of each are grams per hundred grams of rubber. 2b (below).—Zinc oxide required for maximum modulus as a function of TMTD taken (same units). The line has theoretical slope.

be detected at low extents of reaction. This has not yet been quantitatively correlated with crosslinking.

REACTION (6)—OXIDATION OF THE MERCAPTIDE

Given the existence of mercaptan or mercaptide groups as intermediates, their oxidation to disulfides by TMTD (Reaction (6)) is a straightforward consequence. This stage of the reaction is exactly the same as that proposed by Bielstein and Scheele[20]. It has been observed that cetyl mercaptan is rapidly oxidized to the disulfide by TMTD[23,32]. It is well known that TMTD will oxidize sulfide to sulfur[48]. Reaction (6) is written in a form which is non-committal as to the mechanism of the oxidation stage. With some sulfur compounds ionic radical exchange catalyzed by base is extremely rapid compared with free radical oxidation[49]. TMTD reacts more rapidly than simple aliphatic disulfides, but no study of the rate of oxidation of mercaptans by it has been made.

Since the mechanism as outlined requires only two-thirds the TMTD for introduction of crosslinking sulfur and uses the other third for oxidation, it would be predicted that the yield of crosslinks from a given amount of TMTD

TABLE V

EFFECT OF MBTS ON TMTD VULCANIZATION

Formula:

Pale crepe	100
Zinc oxide	10
Zinc laurate	1
TMTD	2
MBTS	Varied

Cure: 24 hours @ 108°

MBTS	200% stesss	MBTS	200% stress
0	105	3.0	115
0.5	110	5.0	150
1.0	115	7.0	180
2.0	120	10.0	210

could be raised by replacing this portion of it by some other oxidizing agent. This technique would be analogous to that used by Barton[7] in his study of high modulus low zinc compounds. The data in Table V show that the modulus of a rubber-TMTD vulcanizate can in fact be raised by adding MBTS to the compound before cure. It may be suggested that this does not establish that

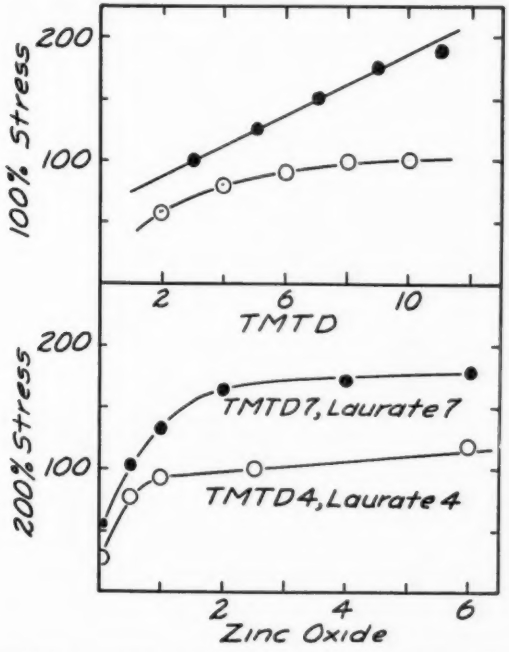
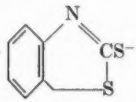


FIG. 3.—Zinc oxide requirements in TMTD vulcanization in the presence of zinc laurate. 3a (above). —Comparison of 100% stress (pounds/in.²) when zinc is supplied entirely as zinc oxide (●) or as zinc laurate (o). 3b (below).—Effect of zinc oxide addition on 200% stress at two levels of zinc laurate. Units grams per hundred of rubber.

MBTS spares TMTD by oxidation of an intermediate, rather than an end product of the vulcanization. It is true that a mixture of rubber, MBTS, and ZnDMDC develops some modulus if heated under the same conditions used to obtain the data of Table V, presumably by the reaction

$$\tfrac{1}{2}\,\text{MBTS} + (CH_3)_2NCS^-{}_2 \longrightarrow \tfrac{1}{2}\,\text{TMTD} + \text{(9)}$$



followed by vulcanization by the usual mechanism. However, this is much slower than the development of modulus by the composition in Table V.

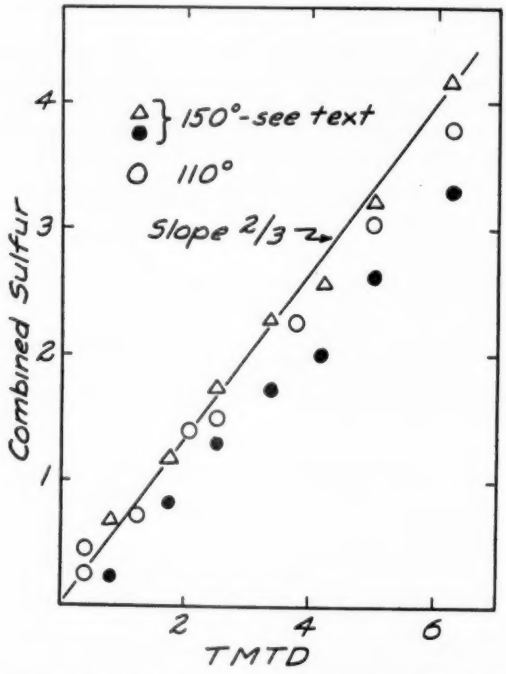


FIG. 4.—Combined sulfur after vulcanization as a function of TMTD taken. Cures at temperatures indicated. Units gram moles TMTD, gram atoms sulfur per 10^4 grams rubber.

REACTION (7)—THE OVERALL STOICHIOMETRY

A number of the stoichiometric relationships set forth in Equation (7) should be susceptible to experimental verification. These include the ratio of reagents and products to crosslinks and to each other and the ratio of sulfur rendered insoluble to crosslinks. Available evidence has been tabulated previously[31] and already discussed in part in previous sections of this report.

Historically the first to be described was the dithiocarbamate formed/TMTD taken ratio, which has received the most detailed attention in the literature. Jarrijon[9] observed that a very high yield of dithiocarbamate is obtained during vulcanization with TMTD. This observation has been thoroughly confirmed[10]; the yield is close to four-thirds equivalents (dithiocarbamate formed) per mole (TMTD taken), independent of temperature.

Other ratios have been examined in less detail. The sulfur combined/crosslink formed ratio was investigated by Gee[2], by Studebaker[3], by Bevilacqua[4], and by Moore[50]. From these results and the present discussion, it is evident an upper limit to this ratio can be set of three (gram atoms/mole). Further ex-

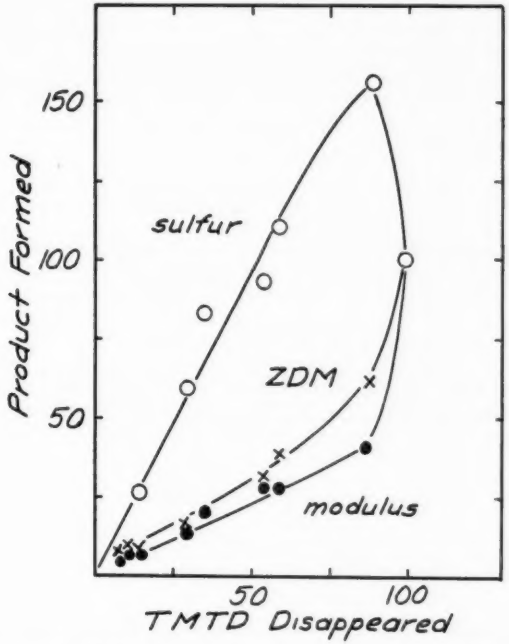


FIG. 5.—Changes in stress, combined sulfur, and dithiocarbamate during cure. Units are in per cent of final value. See text for details.

periments to be described elsewhere confirm a value near two for this ratio in the presence of carbon black.

Barton observed that at low enough temperature little or no "sulfide" sulfur is formed and the combined sulfur approaches two-thirds mole per mole TMTD taken. His results for vulcanization at 110° are compared in Figure 4 with those[4,8] already reported for vulcanization at 150°. The solid points represent analyses for combined sulfur after vulcanization at 150°, the open triangles total sulfur not extracted by chloroform. The difference between these is fully accounted for as sulfide sulfur, determined independently. This emphasizes the alternate modes of decomposition available to TMTD at high temperature

and the attendant difficulty in deciding which observations are directly concerned with the vulcanization reaction.

Other estimates of the ratio of sulfur combined to TMTD taken have been made by Hauser and Brown[25] (0.80 gram atoms/mole), by Moore[50] (0.83), and by Scheele and Hummel[51] (ca. 1.0 using tetraethylthiuram disulfide). The discrepancy between these high values and those reported here and previously is unexplained at the moment, but may reflect varying conditions of vulcanization, or the effect discussed in the second paragraph below.

One unknown product is shown in Equation (7), the thionocarbamate. Compounds of this or related structure have been referred to in the literature but have not been isolated as well characterized compounds[52,53]. If carbonyl sulfide is passed into a solution of dimethylamine and zinc acetate added, a precipitate containing some zinc oxide and a poorly crystallized product which yields carbonyl sulfide on acidification is formed. This is very readily hydrolyzed to yield sulfide. The compound may be thermally unstable, yielding decomposition products which include carbonyl sulfide[54] (or an equimolar mixture of CS_2 and CO_2) and tetramethyl thiourea[17]. Efforts to assay these quantitatively are underway.

EVIDENCE FROM RATES

Unless it is known that all variables controlling reaction rates are adequately controlled, measurements of rates of disappearance of a reagent or appearance of a product cannot give much information concerning a reaction mechanism. One way in which to control extraneous variables is to make comparative measurements with the same reaction mixture, rather than attempt to obtain absolute values for reaction rates. The results of one such experiment are summarized in Figure 5. In this figure the yields of sulfur combined with the rubber, modulus, and dithiocarbamate are plotted as a function of TMTD disappeared from the reaction mixture. A compound was mixed having the formula:

Pale crepe	100
Zinc oxide	10
Zinc laurate	1.5
TMTD	15

and cured in molds in a press for several periods at 108°. The stress-strain properties were measured, and analyses made for combined sulfur, TMTD, and ZnDMDC on each sample after cure. Final values of these after 24 hours were: sulfur 1.25% (theory 1.05%), TMTD 0.12%, ZnDMDC 11.49% (theory 10.18%), stress at 100% elongation 230 pounds per square inch (extrapolated). No sulfide sulfur was found in any sample. The ratios of the values found at each intermediate cure to the final values are plotted in Figure 5.

Two inferences may be drawn from the data: (1) Sulfur enters the polymer as some intermediate which is subsequently converted to crosslinks and (2) the rate of disappearance of TMTD is faster than the rate of appearance of dithiocarbamate and of crosslinks, but the latter two are closely related. The second conclusion was previously reached by Scheele and coworkers[29,55] based on estimation of crosslinks by swelling.

CONCLUSIONS

The mechanism reviewed in some detail here appears adequate to explain substantially all that is now known about vulcanization with TMTD. It has predicted accurately the stoichiometric relationships between the reagents entering into the vulcanization reaction and the known products formed. It presumes that vulcanization is a primary consequence of the interaction of rubber, TMTD, and zinc oxide and not an incidental result. It is not, however, fully established by the evidence now available. In particular the studies by Scheele and coworkers (as exemplified by Reference 33) on the reaction of zinc oxide with thiuram disulfides suggest the interesting possibility that primary attack during vulcanization is on the oxide rather than the hydrocarbon, as assumed in this discussion. There is at present no experimental basis on which to eliminate either of these two alternatives. The success of the mechanism reviewed here in delimiting stoichiometry of the reaction makes it a convenient framework from which to develop a complete understanding of the reaction[56].

SYNOPSIS

The stoichiometric relations between known reagents and products of the vulcanization of rubber with tetramethylthiuram disulfide (TMTD) and zinc oxide have been examined. The results suggest that a stoichiometric reaction does occur. Published speculations concerning the mechanism of TMTD vulcanization are reviewed critically in the light of available evidence.

REFERENCES

[1] The following abbreviations and special conventions are used: TMTD: bis(dimethylthiocarbamoyl) disulfide; TMTM: bis(dimethylthiocarbamoyl) sulfide; MBTS, 2,2'-bis(benzothiazolyl) disulfide; ZnDMDC, zinc dimethyldithiocarbamate. Compound is used in the special sense conventional in the rubber industry to mean the formula for a mixture of rubber with other ingredients which is subjected to cure, the process of exposing to vulcanizing conditions.
[2] Gee, G., *J. Polymer Sci.* **2**, 451 (1947).
[3] Studebaker, M. L., RUBBER CHEM. & TECHNOL. **30**, 1400 (1957).
[4] Bevilacqua, E. M., *J. Polymer Sci.* **28**, 651 (1958).
[5] Bloomfield, G. F., *J. Soc. Chem. Ind.* **68**, 66 (1949).
[6] Barton, B. C., and Hart, E. J., *Ind. Eng. Chem.* **44**, 2444 (1952); Barton, B. C., *J. Polymer Sci.* **18**, 559 (1955).
[7] Barton, B. C., *Ind. Eng. Chem.* **42**, 671 (1950).
[8] Barton, B. C., unpublished. I am indebted to Dr. Barton for permission to quote from his extensive unpublished work on vulcanization.
[9] Dufraisse, C., and Jarrijon, A., *Compt. rend.* **215**, 181 (1942), RUBBER CHEM. & TECHNOL. **17**, 941 (1944); Jarrijon, A., *Rev. gen. caoutchouc* **20**, 155, 177 (1943), RUBBER CHEM. & TECHNOL. **19**, 1061 (1946).
[10] Scheele, W., Lorenz, O., and Dummer, W., *Kautschuk u. Gummi* **7**, WT 273 (1954) and subsequent papers. Reviewed by Scheele, W., *Kolloid Z.* **146**, 14 (1956).
[11] Craig, D., Juve, A. E., and Davidson, W. L., *J. Polymer Sci.* **5**, 709 (1950).
[12] Bruni, G., and Romani, E., *India Rubber J.* **62**, 63 (1921); **64**, 937 (1922); Bruni, G., *ibid.* **62**, 89 (1921).
[13] Maximov, A., *Caoutchouc et guttapercha* **18**, 986 (1921).
[14] Farmer, E. H., *Trans. Faraday Soc.* **38**, 356 (1942).
[15] Moore, C. G., and Watson, W. F., *J. Polymer Sci.* **19**, 237 (1956).
[16] Bergem, N., "Vulcanization", A/S Askim Gummivarefabrik, Askim, Norway, 1957.
[17] Craig, D., Davidson, W. L., and Juve, A. E., *J. Polymer Sci.* **6**, 177 (1951).
[18] Craig, D., Juve, A. E., Davidson, W. L., Semon, W. L., and Hay, D. C., *J. Polymer Sci.* **8**, 321 (1952).
[19] Craig, D., *J. Polymer Sci.* **20**, 197 (1956); RUBBER CHEM. & TECHNOL. **30**, 1291 (1957).
[20] Bielstein, G., and Scheele, W., *Kolloid Z.* **147**, 152 (1956).
[21] Craig, D., Juve, A. E., and Davidson, W. L., *J. Polymer Sci.* **6**, 7 (1951).
[22] Zapp, R. L., Decker, R. H., Dyroff, M. S., and Rayner, H. A., *J. Polymer Sci.* **6**, 331 (1951).
[23] (a) Little, J. R., (b) French, D. M., unpublished.
[24] Bateman, L. C., Glazebrook, R. W., Moore, C. G., and Saville, R. W., *Proc. Third Rubber Technol. Conf.*, London, **1956**, 298; RUBBER CHEM. & TECHNOL. **30**, 397 (1957); Glazebrook, R. W., and Saville, R. W., *J. Chem. Soc.* **1954**, 2094.
[25] Brown, J. R., and Hauser, E. A., *Ind. Eng. Chem.* **30**, 1291 (1938); Hauser, E. A., and Brown, J. R., *ibid.*, **31**, 1225 (1939).
[26] Armstrong, R. T., Little, J. R., and Doak, K. O., *Ind. Eng. Chem.* **36**, 628 (1944).
[27] Farmer, E. H., Ford, J. F., and Lyons, J. A., *J. Appl. Chem.* **4**, 554 (1954).
[28] Shepard, A. F., *Ind. Eng. Chem.* **26**, 1200 (1934).

[30] Lorenz, O., Scheele, W., and Redetsky, W., *Kautschuk u. Gummi* **9**, WT 269 (1956).
[30] Moore, C. G., *J. Chem. Soc.* **1952**, 4232.
[31] Bevilacqua, E. M., *Science* **128**, 840 (1958).
[32] Craig, D., Davidson, W. L., Juve, A. E., and Geib, I. G., *J. Polymer Sci.* **6**, 1 (1951).
[33] Scheele, W., Graseman, H., and Mau, G., *Kautschuk u. Gummi* **10**, 241 (1957).
[34] (a) Ferington, T., and Tobolsky, A. V., *J. Am. Chem. Soc.* **77**, 4510 (1955); (b) *J. Am. Chem. Soc.* **80**, 3215 (1958).
[35] Kern, R. J., *J. Am. Chem. Soc.* **77**, 1382 (1955); Otsu, T., *J. Polymer Sci.* **21**, 559 (1956); **26**, 237 (1957).
[36] (a) Cottrell, T. L., "The Strengths of Chemical Bonds", Butterworths Scientific Publications, London, 1954; (b) Sehon, A. H., and Szwarc, M., *Ann. Rev. Phys. Chem.* **8**, 439 (1957).
[37] Cutforth, H. G., and Selwood, P. W., *J. Am. Chem. Soc.* **70**, 278 (1948).
[38] Walling, C., "Free Radicals in Solution", John Wiley and Sons, Inc., New York, 1957.
[39] Koch, H. P., *J. Chem. Soc.* **1949**, 401.
[40] Brand, J. C. D., and Davidson, J. R., *J. Chem. Soc.* **1956**, 15.
[41] Scheele, W., and Lorenz, O., *Kautschuk u. Gummi* **9**, WT 27 (1956).
[42] Cunneen, J. I., *J. Chem. Soc.* **1947**, 36, 134.
[43] Sears, W. C., *J. Appl. Phys.* **12**, 35 (1941); Sheppard, N., and Sutherland, G. B. B. M., *Trans. Faraday Soc.* **41**, 261 (1945); *J. Chem. Soc.* **1947**, 1699; Sheppard, N., and Simpson, D. M., *Quart. Revs.* **6**, 1 (1952); Salomon, G., and van der Schee, A. Chr., *J. Polymer Sci.* **14**, 181 (1954); Linnig, F. J., and Stewart, J. E., *J. Res. Nat. Bur. Standards* **61**, 9 (1958).
[44] Bevilacqua, E. M., *Rubber Age* (N. Y.) **80**, 271 (1956); *J. Org. Chem.* **21**, 369 (1956).
[45] Tarbell, D. S., and Harnish, D. P., *Chem. Rev.* **49**, 1 (1951).
[46] Craig, D., Juve, A. E., and Davidson, W. L., *J. Polymer Sci.* **5**, 709 (1950).
[47] *Ibid.*, **6**, 13 (1951).
[48] Bedford, C. W., and Sebrell, L. B., *Ind. Eng. Chem.* **14**, 25 (1922); Bedford, C. W., and Gray, Harold, *ibid.*, **15**, 720 (1923).
[49] Bertozzi, E. R., Davis, F. O., and Fettes, E. M., *J. Polymer Sci.* **19**, 17 (1956).
[50] Moore, C. G., *J. Polymer Sci.* **32**, 503 (1958).
[51] Scheele, W., and Hummel, K., *Kautschuk u. Gummi* **10**, WT 267 (1958).
[52] Cummings, A. D., and Simmons, H. E., *Ind. Eng. Chem.* **20**, 1173 (1928).
[53] Jacques, Parrod, *Compt. rend.* **234**, 1062 (1952).
[54] Craig, D., Diller, D., and Rowe, H. E., *J. Polymer Sci.* **28**, 435 (1958).
[55] Scheele, W., Toussaint, H. E., and Stange, R., *Kautschuk u. Gummi* **10**, WT 109 (1957).
[56] This is contribution No. 178 from the Research Center, United States Rubber Company, Wayne, New Jersey.

AGING OF NATURAL RUBBER VULCANIZATES IN THE PRESENCE OF DITHIOCARBAMATES *

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The N,N-disubstituted dithiocarbamates of a wide variety of metals have been suggested as antioxidants for unvulcanized natural rubber[1] and nickel dibutyldithiocarbamate has been incorporated into latex sponge as a protective agent against deterioration caused by light. Pinazzi and coworkers[2] have made an extensive study of the use in natural rubber of nickel dithiocarbamates; they found them capable of protecting some vulcanizates against the crazing produced by light but usually at the expense of an increased sensitivity of thermal aging.

In the present investigation the effects on the rates of thermal and photochemical stress relaxation of natural-rubber vulcanizates of a series of dibutyldithiocarbamates with either metallic or organic cations have been determined. The purposes of the investigation were to determine whether or not the protective action in vulcanizates was restricted to the nickel salt as had been stated[3], but which seemed unlikely in view of the efficacy of other salts in unvulcanized rubber, and, as stress-relaxation measurements are more easily interpreted than conventional aging measurements, to determine as far as possible the protective mechanism.

EXPERIMENTAL

Method.—Stress-relaxation measurements were carried out in the apparatus described in previous publications[4,5], the results being presented as graphs of log (force at time t, f/initial force, f_0) against time t.

Thermal aging measurements were carried out at 100° C in air, using rubber strips 4.0 × 0.5 × 0.05 cm, and measurements of photochemical aging, were made on rubber strips 4.0 × 0.5 × 0.02 cm in oxygen under 365 mμ radiation from a 250-watt compact source (MBQ of B.T.H. Ltd.), filtered by a sheet of Chance OV1 glass.

Preparation of vulcanizates.—The sheets employed were prepared from acetone-extracted deproteinized (D.P.) crepe (supplied by the Indonesian Rubber Research Institute) or pale crepe, into which the vulcanizing ingredients were introduced in an 8 g capacity internal mixer[6]. The compounded rubber was vulcanized in a 50-ton press in a small mold provided with spacers to give 10 cm square sheets of the desired thickness. The recipes employed for the vulcanizates were as follows:

Peroxide vulcanizate: D.P. crepe 100 parts; dicumyl peroxide 3 parts.
Cure time 35 minutes at 140° C.

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 34, pages 228–236 (1958).
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Santocure vulcanizate: Pale crepe 100 parts; zinc oxide 5 parts; sulfur 2.5 parts; stearic acid 1.0 part; Santocure (N-cyclohexyl-2-benzothiazolyl sulfenamide) 0.7 part.
Cure time 25 minutes at 140° C.

TMTD vulcanizate: D.P. crepe 100 parts; zinc oxide 2.0 parts; stearic acid 1.0 part; TMTD (tetramethylthiuram disulfide) 4.0 parts.
Cure time 45 minutes at 140° C.

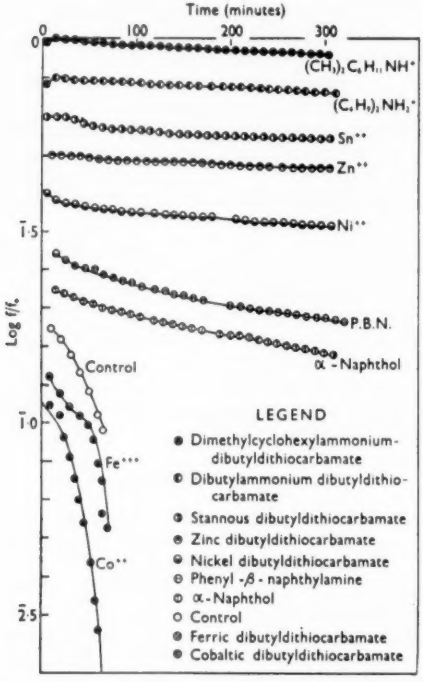


FIG. 1.—Stress relaxation of dicumyl peroxide vulcanizate at 100° C, in presence of dibutyldithiocarbamates.

All the vulcanizates were extracted with hot acetone for 8 hours and dried in vacuo before use, except those to be used in experiments conducted on unextracted TMTD vulcanizates.

Additives were introduced by swelling the strips overnight in an ethyl acetate solution and removing the solvent in vacuo. In the data recorded below the concentrations given are those of the solutions. The additive concentrations in the rubber should be of the same order, since the vulcanizates imbibed some 80 per cent of their own weight of ethyl acetate, while some measurements of the actual concentration of PBN introduced into a vulcanizate

by swelling indicated that there was up to 20 per cent more present than was calculated, assuming that the relative weights of additive and ethyl acetate were the same in the swollen vulcanizate as in the original solution.

Materials.—Dibutyldithiocarbamates of nickel, copper, iron, cobalt and cadmium were prepared and purified by Mr. G. Higgins and Mr. E. D. Farlie, from dibutylamine, carbon disulfide and the appropriate oxide. The corresponding barium, lead and stannous salts were obtained by double decomposition between the metal chlorides and an aqueous solution of sodium dibutyldithiocarbamate ("Tepidone"—Du Pont Ltd.), the precipitated salts being filtered off and washed with a little acetone. Samples of zinc and dibutylammonium dibutyldithiocarbamate and the ethyl, octyl and benzyl esters of dibutyldithiocarbamic acid were kindly donated by Monsanto Ltd., and dimethylcyclohexylammonium dibutyldithiocarbamate was used as the commercial 50 per cent solution (R.Z.50A—Monsanto Ltd.). The barium, lead and zinc dibutyldithiocarbamates, zinc diethyldithiocarbamate (ZnDMDC) and zinc dimethyldithiocarbamate (methasan—Monsanto Ltd.) were purified by twice recrystallizing from hot acetone.

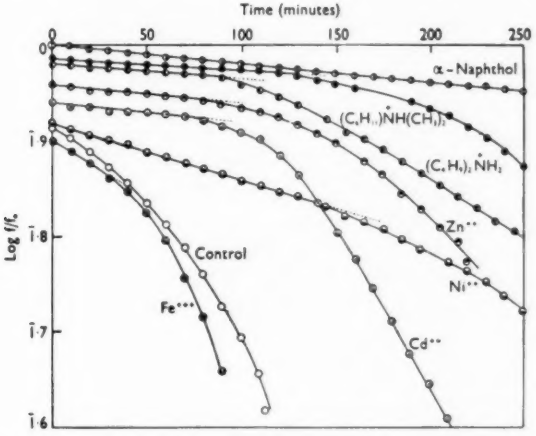


FIG. 2.—Stress relaxation of dicumyl peroxide vulcanizate under 365 mμ illumination, in presence of dibutyldithiocarbamates.

RESULTS

In Figures 1 to 6 are shown the results of stress-relaxation measurements during thermal and photochemical aging of the three different natural-rubber vulcanizates (peroxide, santocure-accelerated sulfur and TMTD-sulfurless vulcanized) in the presence of the various dithiocarbamates. Dithiocarbamates were introduced into all the rubber strips used in thermal aging experiments and into strips of TMTD vulcanizate used for photochemical aging from 0.2 per cent solutions of the metal salts or 0.3 per cent solutions of the amine salts (roughly 4.3×10^{-3} molar); dithiocarbamate and also 1-naphthol were introduced into the remaining strips used for photochemical aging from solutions accurately 1.74×10^{-3} molar.

In peroxide and TMTD sulfurless vulcanizates all the dibutyldithiocarbamates used, except the cobalt and iron salts, were powerful retarders of stress relaxation whether this was induced by heat or by u.v. light. Against thermal aging the dithiocarbamates were considerably more efficient, in terms of reduction of rate of stress decay, than equal weight concentrations of the commonly used phenyl-2-naphthylamine or of 1-naphthol (Figures 1 and 5). Against photochemical aging the dithiocarbamates in general gave a reduction in rate of the same order as, or slightly greater than, that given by an equimolar concentration of 1-naphthol but were apparently more rapidly used up, for the

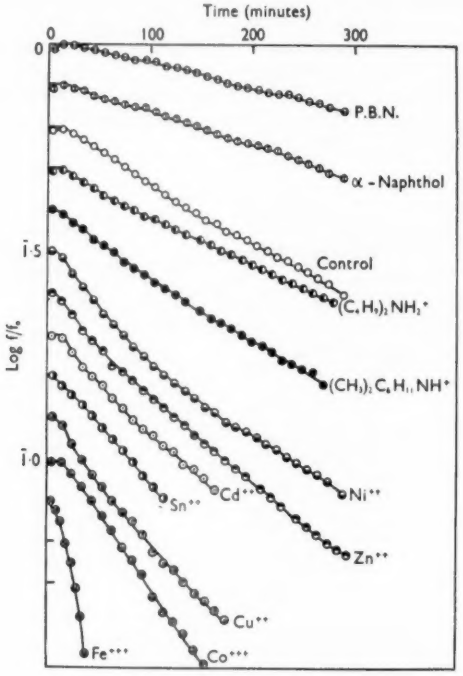


FIG. 3.—Stress relaxation of santocure vulcanizate at 100° C, in presence of dibutyldithiocarbamates.

acceleration in rate observed when a retarder is exhausted appeared sooner with these compounds than with 1-naphthol (Figures 2 and 6). The iron and cobalt salts gave contradictory results, sometimes behaving as retarders and under other conditions acting as promoters of stress-decay, perhaps due to competing reactions differently favored by change in conditions. These two salts, although prepared by double decompositions involving the bivalent cation, gave analytical values corresponding to salts of the trivalent cation.

With the santocure-accelerated vulcanizate only the dibutylammonium dibutyldithiocarbamate showed any sign of acting as an antioxidant either

thermally or photochemically. In the presence of all the other dithiocarbamates stress relaxation was at least as rapid as that of the control (Figures 3 and 4).

Measurements made on the rate of photolytic stress relaxation of a peroxide vulcanizate in the presence of the ethyl, octyl and benzyl esters of di-isobutyldithiocarbamic acid, introduced in the usual way from 1.7×10^{-3} molar solution, showed that these additives had no protective effect but indeed had a slight accelerating influence (Figure 7). The protective action of the dithiocarbamate salts must therefore be attributed specifically to the anion.

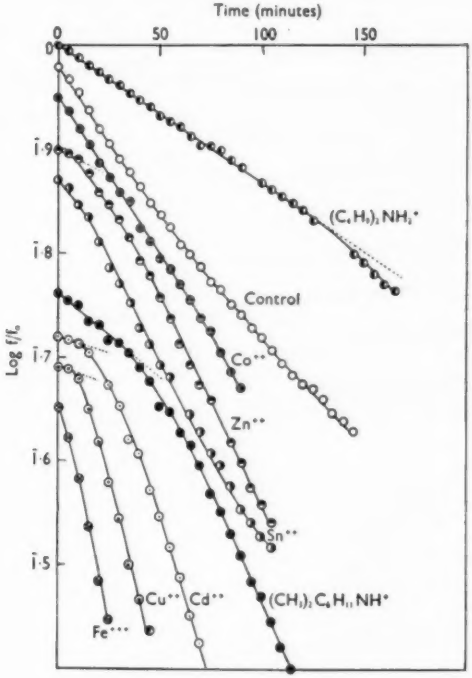


FIG. 4.—Stress relaxation of santocure vulcanizate under 365 mμ illumination, in presence of dibutyldithiocarbamates.

As is well known, purified olefins oxidize by a chain mechanism in which the reaction chains are initiated by the breakdown of previously formed hydroperoxide and it has been shown[7] that in purified polyisoprene this oxidative reaction is accompanied by degradation. The mechanism of oxidative degradation of rubber vulcanizates is, however, still far from clear but it is usually assumed that a similar mechanism is operative. Recently, evidence has been obtained[5] which gives considerable support for a mechanism of this type being responsible for the oxidative degradation of peroxide rubber in light of the near ultraviolet. It has been pointed out[8] that a peroxide-initiated chain process

may be susceptible to two different types of inhibition or retardation: by removal of the chain-carrying free radicals or by removal of the peroxide initiators. The first mechanism is probably responsible for the retarding action of the conventional antioxidants of the amine and phenol types. The second mode of inhibition has been suggested[9] for a number of mineral oil antioxidants which include zinc dibutyldithiocarbamate. The suggestion that the antioxidant effect of the dibutyldithiocarbamate ion may be due to decomposition of hydroperoxide is reinforced by the observation that addition at room temperature of excess cumyl hydroperoxide to ethyl acetate solutions of cupric and

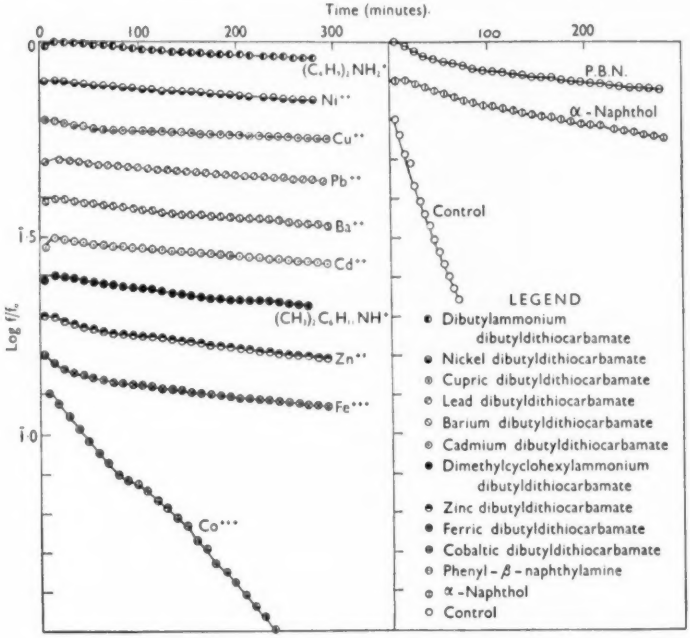


FIG. 5.—Stress relaxation of TMTD (sulfurless) vulcanizates at 100° C, in presence of dibutyldithiocarbamates.

nickel dibutyldithiocarbamates led, within a few minutes, to discharge of the color and formation of a precipitate.

The marked difference between the behavior of dithiocarbamates in the sulfurless vulcanizates and the accelerated sulfur vulcanizate is not surprising in view of the differences in network structure. Santocure vulcanizates contain more combined sulfur per crosslink than TMTD sulfurless vulcanizates[10], and this additional sulfur is involved in types of structure not found in the TMTD vulcanizates, e.g., cyclic sulfides and, probably, polysulfide crosslinks.

Replacement of the butyl groups of the dibutyldithiocarbamate by ethyl or methyl groups has little effect on the antioxidant power as is shown in Figures 8 and 9 in which are compared the rates of relaxation of strips of extracted

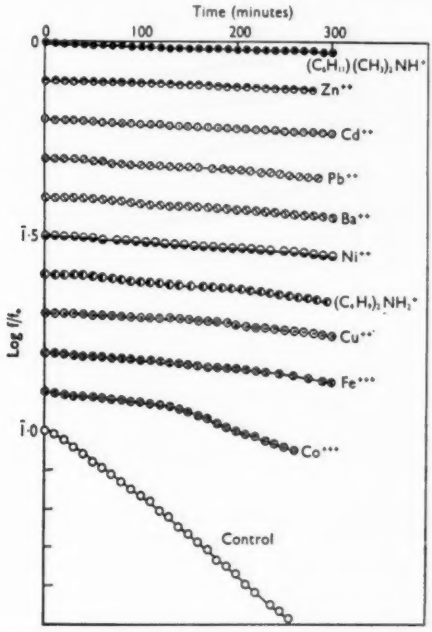


FIG. 6.—Stress relaxation of TMTD (sulfurless) vulcanizate under 365 mμ illumination, in presence of dibutyldithiocarbamates.

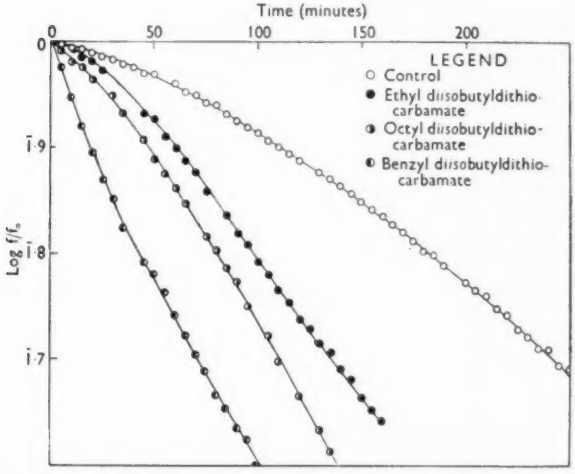


FIG. 7.—Stress relaxation of dicumyl peroxide vulcanizate under 365 mμ illumination, in presence of esters of diisobutyldithiocarbamic acid.

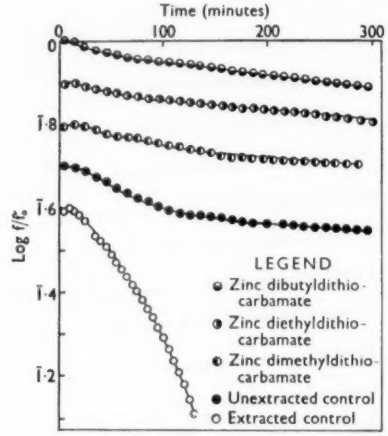


FIG. 8.—Stress relaxation, at 100° C, of TMTD (sulfurless) vulcanizate containing the zinc salts of various dialkyldithiocarbamates, and of an unextracted TMTD (sulfurless) vulcanizate.

TMTD-sulfurless vulcanizate which contained zinc dimethyl-, zinc diethyl- and zinc dibutyldithiocarbamates. The dimethyl compound appears to be slightly less effective, but this is probably due to its being in a lower concentration in

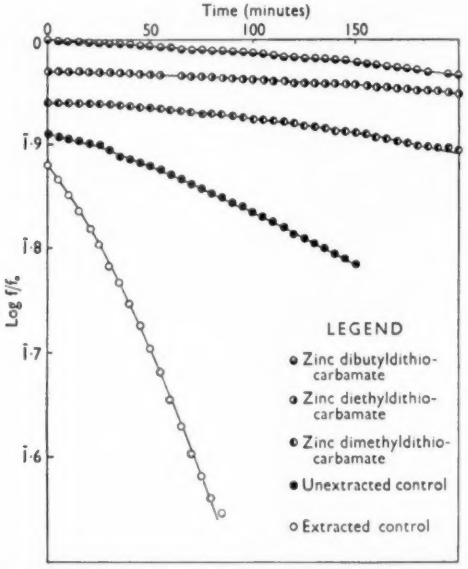


FIG. 9.—Stress relaxation, under 365 mμ illumination, of TMTD (sulfurless) vulcanizate containing the zinc salts of various dialkyldithiocarbamates, and of an unextracted TMTD (sulfurless) vulcanizate.

the rubber as it is insufficiently soluble in ethyl acetate to yield a 0.2 per cent solution.

The extracted TMTD-sulfurless vulcanizates used in this investigation did not show the outstanding aging attributed to this class of vulcanizate. In fact the extracted santocure accelerated vulcanizate relaxed less rapidly (compare controls of Figures 3 and 5). As it is known that zinc dimethyldithiocarbamate equivalent to two-thirds of the original tetramethylthiuram disulfide can be extracted from a TMTD vulcanizate[11], one of our colleagues, Mr. S. G. Fogg, has suggested that it is this dithiocarbamate which is responsible for the good aging found for TMTD vulcanizates in practice. Such an idea is supported by the observation that the stress relaxation of an unextracted TMTD sulfurless vulcanizate is much slower than that after extraction (Figures 8 and 9).

SUMMARY

The thermal and photochemical aging of extracted dicumyl peroxide-, TMTD (sulfurless)- and santocure-vulcanized rubber, in presence of a number of metal and alkylammonium dithiocarbamates, has been investigated by measurements of stress relaxation. The dithiocarbamates have a considerable protective action upon the degradation of peroxide- and TMTD-vulcanizates, but they accelerate stress decay in santocure-accelerated vulcanizates. The reasons for this behavior are discussed. It is suggested that the excellent aging properties of unextracted TMTD vulcanizates are due to the presence of zinc dimethyldithiocarbamate formed during vulcanization.

ACKNOWLEDGMENTS

The authors are indebted to Dr. W. F. Watson for much helpful advice, and also to Mr. R. Tiller and Miss G. Long for assistance in the experimental measurements.

REFERENCES

[1] Bemmels, C. W. (to Industrial Tape Corporation), U. S. Patent 2,615,059.
[2] Pinazzi C., Billuart M., and Karmitz, P., *Rev. nickel* **22**, 11 (1956).
[3] Sanders, P. A., and Vincent, J. R. (to Du Pont de Nemours & Co.), U. S. Patent 2,538,047.
[4] Berry, J. P., *Trans. Inst. Rubber Ind.* **32**, 224 (1956).
[5] Dunn, J. R., Scanlan, J., and Watson, W. F., *Trans. Faraday Soc.* **54**, 730 (1958).
[6] Wilson, D., and Watson, W. F., *Rubber and Plastics Age* **38**, 982 (1957).
[7] Morris, A. L., Ph.D. Thesis, London, 1952.
[8] Kennerly, G. W., and Patterson, W. L., *Ind. Eng. Chem.* **48**, 1917 (1956).
[9] Harle, O. L., Paper presented to A.C.S. Division of Petroleum Chemistry, Miami, April, 1957.
[10] Ross, G., and Moore, C. G., Unpublished results.
[11] Scheele, W., Lorentz, O., and Dummer, W., *Kautschuk u. Gummi* **7**, WT 273 (1954); RUBBER CHEM. & TECHNOL. **29**, 1 (1956).

THERMAL DEGRADATION OF POLYACRYLONITRILE, POLYBUTADIENE, AND COPOLYMERS OF BUTADIENE WITH ACRYLONITRILE AND STYRENE *

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INTRODUCTION

The copolymers, styrene-butadiene (GR-S) and acrylonitrile-butadiene (nitrile rubber), currently designated in the technical literature as SBR and NBR, respectively, represent two of the more important synthetic rubbers. This paper describes the results of an investigation of the relative thermal stability and of the products of degradation obtained when these rubbers are pyrolyzed in a vacuum. A similar description is given of the thermal behavior of polyacrylonitrile and polybutadiene.

Details of the method employed in this investigation have been described previously[1–5]. The method consists of two parts. In the first part, a sample weighing 25 to 50 mg is heated in a vacuum, first for 5 min during a heating-up period, then for 30 min at a constant temperature; the residue is weighed, and the volatile products fractionated. The fractions are then weighed and analyzed in the mass spectrometer or tested for average molecular weight by a microcryoscopic method. In the second part, a 4 to 5 mg sample in a platinum crucible suspended from a very sensitive tungsten spring balance[3] is heated in a vacuum, and the rate of loss of weight of the sample is observed at intervals. The activation energy of degradation is calculated from the initial rates by using the Arrhenius equation.

THERMAL DEGRADATION OF POLYBUTADIENE AND SBR

A study of the relative thermal stability of polybutadiene and the copolymer SBR, and of yields and chemical nature of the products resulting from pyrolysis of these two materials, has been reported previously[2,4]. Polybutadiene was found to be more stable than the copolymer. The ratios of small molecular fragments to large ones were 14:84 for polybutadiene and 12:88 for SBR.

In this investigation a study was made of rates of thermal degradation of these two substances by the loss-of-weight method, using a very sensitive tungsten spring balance enclosed in a vacuum[3]. Samples of polybutadiene and of SBR (76.5% of butadiene and 23.5% of styrene), weighing about 5 mg, were used. The materials were prepared by purifying commercial products using a method which has been described previously[2].

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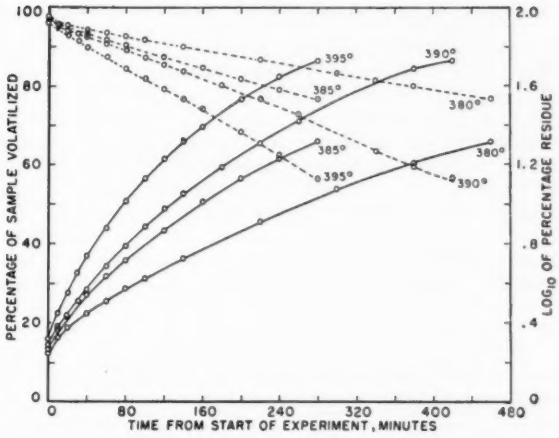


FIG. 1.—Thermal degradation of polybutadiene. Solid lines represent percentage volatilization versus time and dashed lines represent logarithm of percentage residue versus time.

Results of rate studies for polybutadiene are shown in Figure 1. About 12 to 16 per cent of the samples was vaporized at zero time; this vaporization took place during the approximately 15 min heating-up period. Zero time in these experiments was reckoned from the moment the sample had reached the operating temperature. The fact that the logarithm of percentage residue versus time curves deviate only slightly from straight lines indicates that the reaction involved in the thermal degradation of polybutadiene approaches first order.

In Figure 2 rate of volatilization is plotted versus amount volatilized. The apparent initial rates are obtained by extrapolating the straight parts of the rate curves to the ordinate. These rates, in percentage of sample per minute, are 0.21, 0.31, 0.42, and 0.63 for temperatures 380°, 385°, 390°, and 395° C, respectively. On plotting logarithm of the initial rates versus the inverse of

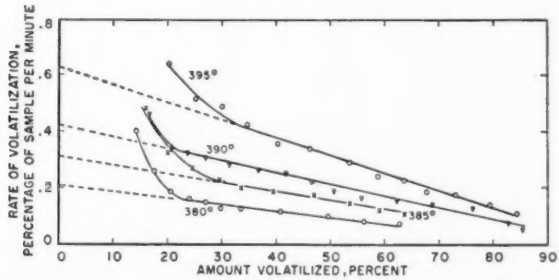


FIG. 2.—Rates of volatilization of polybutadiene. Solid lines represent percentage volatilization versus time and dashed lines represent logarithm of percentage residue versus time.

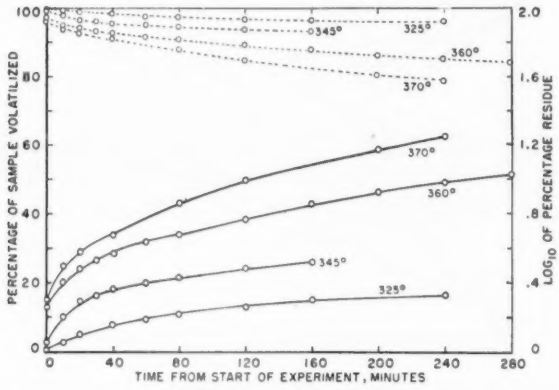


FIG. 3.—Thermal degradation of SBR. Solid lines represent percentage volatilization versus time and dashed lines represent logarithm of percentage residue versus time.

absolute temperature, a straight line is obtained, whose slope indicates an activation energy of 62 kcal/mole.

Percentage volatilization of SBR versus time is shown plotted in Figure 3 (solid lines). Here again there is considerable loss of weight during the heating-up period. Plots of logarithm of percentage residue versus amount volatilized (dashed lines) deviate considerably from straight lines. The reaction involved in the thermal degradation of SBR appears to be more complicated than that for polybutadiene and the reaction is far from first order. Rate of volatilization versus amount volatilized is shown in Figure 4. The rates, very high initially, drop rapidly with extent of volatilization. It is not possible to determine with any accuracy the activation energy from these rate curves.

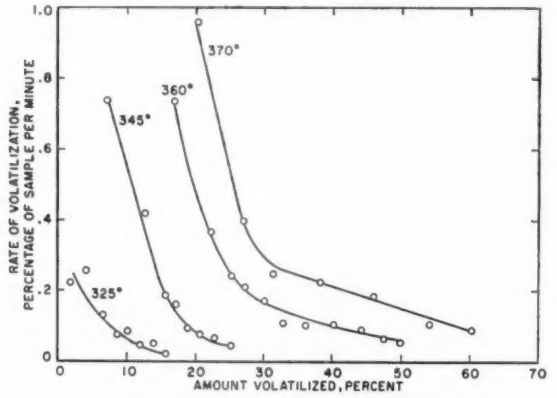


FIG. 4.—Rates of volatilization of SBR.

THERMAL DEGRADATION OF POLYACRYLONITRILE AND NBR

The polyacrylonitrile[14] of high purity and in the form of a fine white powder, had a number-average molecular weight of about 40,000. The NBR rubber was Goodrich Hycar 1042 consisting of about 30 per cent of acrylonitrile and 70 per cent of butadiene. The rubber was extracted for 24 hr with ethanol-toluene azeotrope in order to remove impurities. It was then kept in a vacuum at 60 to 70° C for 5 hr. The purified material analyzed 8.2 per cent of nitrogen, which corresponds to 31 per cent of acrylonitrile. Specimens of polyacrylonitrile and NBR were heated prior to pyrolysis, in a vacuum at 110° C to a constant weight.

Results of pyrolysis are shown in Table I. Fraction V_{-190} represented less than 0.1 per cent of the total volatilized and is not shown in this table. For definition of fractions see footnote to Table I. As in the case of many other polymers the ratio $V_{25}:V_{pyr}$ remained constant throughout the temperature range. On the average, this ratio is 12:88 in the case of polyacrylonitrile, and 14:86 in the case of NBR. In the latter case, in calculating the average ratio, results of Experiment 1 were excluded, because volatilization was only 9 per cent.

As seen from Table I, volatilization of polyacrylonitrile stabilizes at about 70 to 73 per cent. This is in agreement with the work of Kern and Fernow[6], who found that dry distillation of this material was accompanied by carboniza-

TABLE I

PYROLYSIS OF POLYACRYLONITRILE AND NBR

Experiment number	Temperature, °C	Volatilization, %	Volatile fractions[a] based on total volatilized	
			V_{pyr}, %	V_{25}, %
		Polyacrylonitrile		
1	250	21.5	86.3	13.7
2	250	20.7	89.1	10.9
3	250	18.0	89.0	11.0
4	275	34.9	88.0	12.0
5	300	46.6	86.3	13.7
6	325	53.4	88.4	11.6
7	325	52.3	88.6	11.4
8	325	49.7	87.4	12.6
9	325	50.6	88.8	11.2
10	350	57.7	88.7	11.3
11	350	57.9	87.8	12.2
12	400	67.7	90.1	9.9
13	425	70.2	87.2	12.8
14	455	72.8	88.3	11.7
Average	—	—	88.1	11.9
		NBR		
1	310	9.1	74.0	26.0
2	350	29.4	84.5	15.5
3	365	64.5	87.8	12.2
4	380	80.0	84.7	15.3
5	400	95.0	84.8	15.2
Avg. (2 to 5 incl.)	—	—	85.5	14.5

[a] The following volatile fractions were collected: V_{pyr}, volatile at the temperature of pyrolysis, but not at 25° C; V_{25}, volatile at 25° C, but not at −190°. In the case of other polymers it was usually found necessary to separate this fraction into two parts to facilitate mass spectrometer analysis. Here it was found unnecessary to do so; V_{-190}, volatile at −190° C.

TABLE II

MASS SPECTROMETER ANALYSIS OF V_{25} FROM PYROLYSIS OF POLYACRYLONITRILE

	Time interval between end of experiment and analysis									
	1 to 2 hours						1 day		1 week	
Component	Expt. 1,[a] mole %	Expt. 4, mole %	Expt. 5, mole %	Expt. 11, mole %	Expt. 13, mole %	Expt. 14, mole %	Expt. 2, mole %	Expt. 7, mole %	Expt. 3, mole %	Expt. 8, mole %
Hydrogen cyanide	34	22	16	68	66	63	—	28	—	—
Acrylonitrile	36	45	49	10	7	6	—	—	—	—
Vinylacetonitrile	30	30	32	13	13	12	88	63	86	59
Pyrrole	—	3	3	—	—	—	12	—	14	—
Acetonitrile	—	—	—	3	6	10	—	—	—	22
Butyronitrile	—	—	—	2	—	3	—	—	—	—
Propionitrile	—	—	—	4	8	6	—	9	—	19
Total	100	100	100	100	100	100	100	100	100	100

[a] Experiment numbers are the same as those given in Table I.

tion of the residue. A possible explanation of this stabilization, as given by McCartney[7] and Houtz[8], is the formation, along the chain, of ring structures involving nitrogen from the CN groups. NBR, which contains only 31 per cent of acrylonitrile, does not show any stabilization through the entire temperature range.

Fractions V_{pyr} from polyacrylonitrile and NBR had a tan waxlike appearance. They were not readily soluble in ordinary organic solvents, including pyridine. Average molecular weight by the microcryoscopic method in diphenylamine was 300 ± 9 for polyacrylonitrile and 401 ± 3 for NBR.

Fraction V_{-190} from pyrolysis of polyacrylonitrile was analyzed in the mass spectrometer. This fraction consisted of hydrogen. The V_{-190} fraction from NBR was too small for analysis.

Fraction V_{25} from pyrolysis of polyacrylonitrile when first collected was a milky-white liquid. The color of the liquid changed after standing, first to tan and then to brown. Results of mass spectrometer analysis of this fraction are shown in Table II. V_{25} fractions that collected in experiments 1, 4, 5, 11, 13, and 14 were analyzed within 1 to 2 hours after they were collected. The time interval between collection and analysis was 1 day for Experiments 2 and 7, and 1 week for Experiments 3 and 8.

The main constituents in V_{25} are HCN, acrylonitrile, and vinylacetonitrile. The composition of V_{25} seems to depend on the time interval elapsing between pyrolysis and analysis. This suggests the possibility that some of the components, particularly HCN and acrylonitrile, react and become nonvolatile on standing and, as a result, the remaining volatile constituents become accentuated in the analysis. This could explain why Houtz[8] reported that pyrolysis at 400° C yielded only a trace of HCN. On the other hand, Hideo Nagao and coworkers[9] reported the evolution of a considerable amount of HCN when polyacrylonitrile was heated at temperatures from 200° to 350° C in an atmosphere

TABLE III

MASS SPECTROMETER ANALYSIS OF V_{25} FROM PYROLYSIS OF NITRILE RUBBER

Formula of component	Average of 4 analyses, mole %
C_2H_4	9.1
C_2H_6	4.7
C_3H_4	3.0
C_3H_6	2.9
C_4H_6	14.1
C_4H_8	8.3
C_4H_{10}	3.3
C_5H_6	2.5
C_5H_8	9.1
C_5H_{10}	4.8
C_5H_{12}	1.6
C_6H_6	4.3
C_6H_8	6.6
C_6H_{10}	5.4
C_6H_{12}	2.7
C_7 to C_{10} inclusive	17.6
Total	100.0

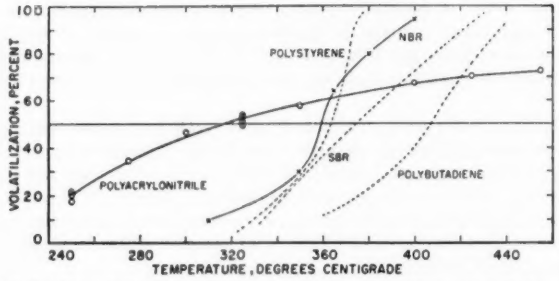


FIG. 5.—Relative thermal stability of polymers and copolymers. Curves for polystryene, SBR, and polybutadiene were taken from Figure 4 of Reference 4. The T_4 values are as follows: 407° C for polybutadiene, 374° C for SBR, 364° C for polystyrene, 360° C for NBR, and 316° C for polyacrylonitrile.

of air or nitrogen. Burlant and Parsons[10] found ammonia as one of the decomposition products from pyrolysis of polyacrylonitrile. We could not find ammonia in the volatiles.

Results of mass spectrometer analysis of V_{25} from NBR are shown in Table III. Two of the analyses were made shortly after the fractions were collected and kept at the temperature of liquid N_2, a third one after an interval of 3 days at room temperature, and a fourth one after an interval of 8 days at the same temperature. All the analyses were similar and the average results are shown in Table III. The results resemble those obtained previously for butadiene and SBR (formely GR-S)[2]. It is rather surprising that none of the products characteristic of polyacrylonitrile pyrolysis showed up in these analyses, although two of the analyses were made shortly after the fractions were prepared and were kept in liquid N_2 until the time of analysis. It is likely that in the presence of unsaturated fragments resulting from pyrolysis of the butadiene in the copolymer, the hydrogen cyanide, acrylonitrile, and vinylacetonitrile, polymerize more rapidly than in their absence, and therefore do not show up in the analysis of the acrylonitrile-butadiene copolymer.

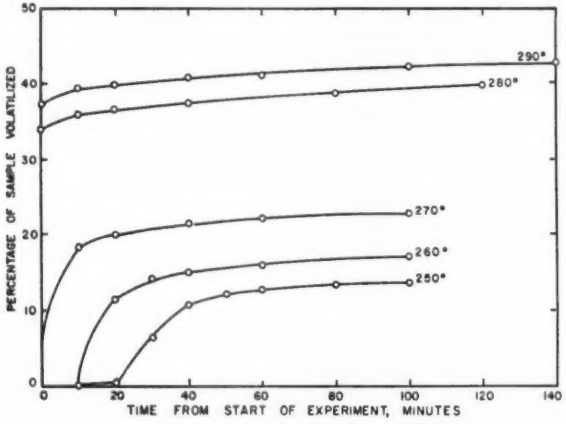


FIG. 6.—Thermal degradation of polyacrylonitrile.

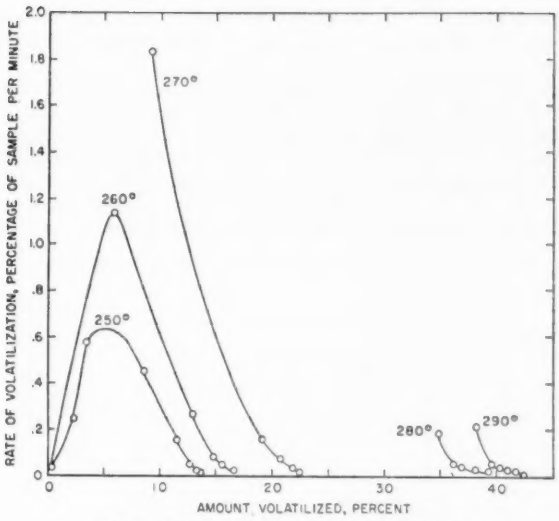


FIG. 7.—Rates of volatilization of polyacrylonitrile.

A comparison of thermal stabilities of the various polymers and copolymers discussed in this paper, and also of polystyrene, is shown in Figure 5. The curves for polyacrylonitrile and NBR are based on data in Table I, and those for polystyrene, SBR, and polybutadiene were taken from Figure 1 of Reference

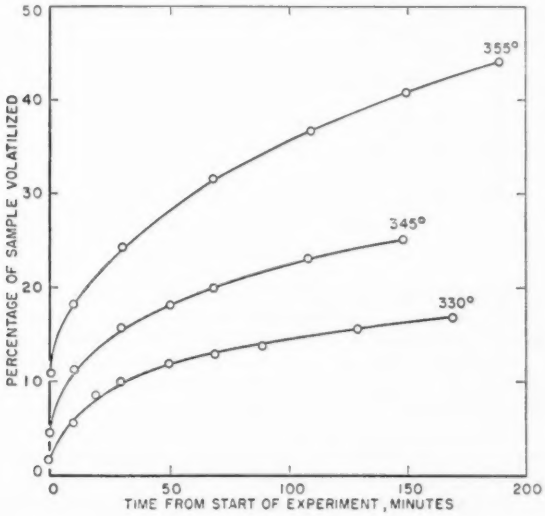


FIG. 8.—Thermal degradation of NBR.

4. The temperature, T_h° C, at which the sample loses half of its weight by vaporization in 35 min, can serve as a basis of comparison of thermal stability of polymers.

Results of rate studies in the tungsten spring balance are shown for polyacrylonitrile in Figures 6 and 7. In Figure 6, percentage of volatilization is plotted versus time from start of experiment. At lower temperatures, a considerable initiation period is observed. Beyond this period volatilization proceeds rapidly, but soon drops to a very small value, indicating stabilization of the residue. At higher temperatures the initiation period terminates during the 15-min heating-up period and the curves show stabilization of the polymer soon

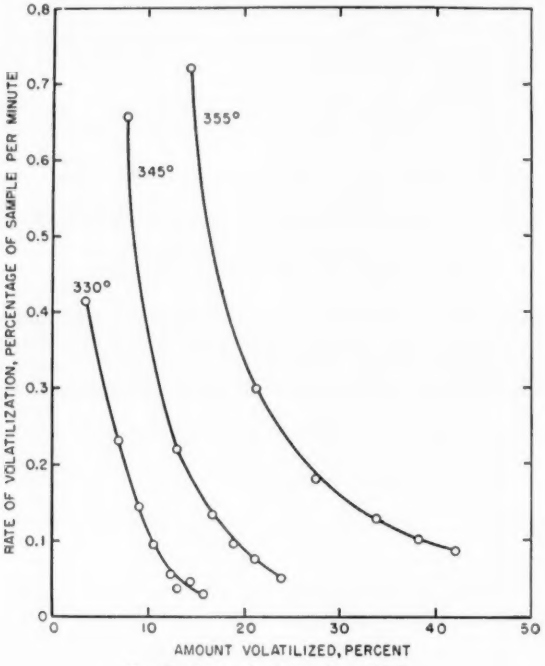


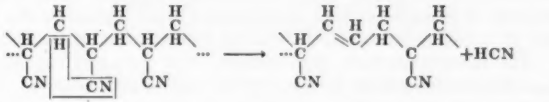
FIG. 9.—Rates of volatilization of NBR.

after the sample reaches the operating temperature. These facts can be observed more easily in Figure 7, where rate of volatilization in per cent of the original sample per minute is plotted against percentage volatilization. It is not possible to estimate with any degree of accuracy the initial rates or the activation energy based on any of the rates shown in Figure 7.

Results of rate studies for NBR are shown plotted in Figure 8, where percentage volatilization is plotted versus time from start of experiment, and in Figure 9, where rate of volatilization in per cent of original sample per minute is plotted versus percentage volatilization. The two sets of curves resemble closely those for SBR shown above (Figures 3 and 4), and no definite conclusion as to initial rates and activation energy can be based on these curves.

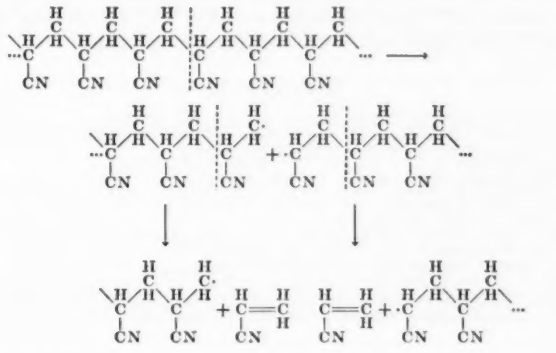
DISCUSSION

The main constituents of the light volatile fraction V_{25} obtained in the pyrolysis of polyacrylonitrile, are hydrogen cyanide, acrylonitrile, and vinylacetonitrile. The hydrogen cyanide most likely forms by splitting-off the chain in the same manner as CH_3COOH in the pyrolysis of polyvinyl acetate[11], HCl in the pyrolysis of polyvinyl chloride[12], and HF in the pyrolysis of hydrofluoroethylene polymers[13].



(1)

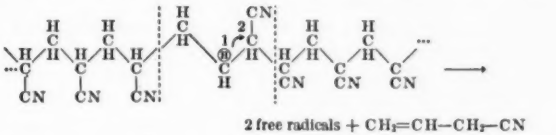
Formation of monomer can be visualized as follows. A random scission of a C—C bond in the chain results in two free radical ends.



(2)

This is followed by an unzipping reaction yielding monomers, as shown in Equation (2).

Formation of vinylacetonitrile could be explained if we assume a head-to-head arrangement at some positions in the chain, as shown in Equation (3).



(3)

This formation involves 2 C—C scissions in the chain, followed by a hydrogen transfer from position 1 to position 2.

The pyrolysis curves for polyacrylonitrile (Figure 5) as well as the rate curves (Figures 6 and 7) show stabilization during pyrolysis. This is characteristic of polymers in which the loss of side groups from adjacent carbons of the chain results in conjugated double bonds in the chain, since these double bonds tend to enhance the thermal stability of the chain. Polyvinyl chloride[12] and polyvinylidene fluoride[13] may be cited as examples of a behavior similar to that of polyacrylonitrile.

ABSTRACT

Polybutadiene and a copolymer consisting of 76.5 per cent butadiene and 23.5 per cent of styrene were investigated as to the rate of their thermal degradation. The rates for polybutadiene indicated an activation energy of 62 kilocalories per mole. The copolymer had very high initial rates of degradation followed by a rapid drop, so that it was not possible to obtain a reliable activation energy.

Polyacrylonitrile and a copolymer consisting of 31 per cent of acrylonitrile and 69 per cent of butadiene were investigated with regard to the nature and distribution of volatile products, as well as to the rates of their thermal degradation. The rates were very high initially, but dropped rapidly so that it was not possible to determine accurately the activation energy. The acrylonitrile-butadiene copolymer showed a decomposition pattern similar to that of polybutadiene. Here, too, the activation energy could not be deduced accurately from the rate curves. Comparative thermal stability in terms of temperature, at which half of the polymer sample is evaporated in 35 minutes of heating, is as follows: 407° C for polybutadiene, 374° C for SBR, 364° C for polystyrene, 360° C for NBR, and 316° C for polyacrylonitrile.

REFERENCES

[1] Madorsky, S. L., and Straus, S., *J. Research NBS* **40**, 417 (1948); RP1886.
[2] Madorsky, S. L., Straus, S., Thompson, D., and Williamson, I., *J. Research NBS* **42**, 499 (1949); RP1989.
[3] Madorsky, S. L., *J. Polymer Sci.* **9**, 133 (1952); **11**, 491 (1953).
[4] Straus, S., and Madorsky, S. L., *J. Research NBS* **50**, 165 (1953); RP2405.
[5] Straus, S., and Madorsky, S. L., *Ind. Eng. Chem.* **48**, 1212 (1956).
[6] Kern, W., and Fernow, H., *J. prakt. Chem.* **160**, 281 (1942); RUBBER CHEM. & TECHNOL. **17**, 356 (1944).
[7] McCartney, J., "Polymer Degradation Mechanisms", NBS Circ. 525, 123 (1950).
[8] Houtz, R., *Textile Research J.* **20**, 786 (1950).
[9] Nagao, Hideo, Uchida, Moriya, and Yamaguchi, Teruo, *Kogyo Kagaku Zasshi* **59**, 698 (1958).
[10] Burlant, W. J., and Parsons, J. L., *J. Polymer Sci.* **22**, 249 (1956).
[11] Grassie, N., *Trans. Faraday Soc.* **48**, 379 (1952); **49**, 835 (1953).
[12] Stromberg, R. R., Straus, S., and Achhammer, B. G. (unpublished paper).
[13] Madorsky, S. L., Hart, V. E., and Straus, S., *J. Research NBS* **51**, 327 (1953); RP2461.

[14] The authors are indebted to C. A. Sperati of the Polychemicals Department, E. I. du Pont de Nemours and Co., for supplying them with this polymer, which is used in the production of Orlon fiber.

THE DEGRADATION OF ELASTOMERS. 2. OXIDATIVE DEGRADATION OF NATURAL RUBBER VULCANIZATES AT DIFFERENT ELONGATIONS AND TEMPERATURES. II *

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INTRODUCTION

When thin filaments or strips of a vulcanizate are stretched to some arbitrary value, there is observed at constant T a slow, progressive reduction in the value of the force which is necessary to maintain the original elongation; this is usually referred to as stress relaxation[1]. The process is unusually sensitive and can be measured with a high degree of accuracy. It has also been referred to[2] as a "chemo-rheological process," a term which stresses the idea that the gradual reduction in the tension at constant temperature and elongation, at least in the higher temperature ranges, has its origin in a chemical degradation of the macromolecular network. Fundamentally, the C—C main chain bonds may be broken, or the sulfur bridges may be cleaved. Hence, measurements of the rate of relaxation give information on the stability of vulcanizates in oxygen or air. In our efforts to realize experimental conditions for which the change in relative force required to maintain a chosen elongation runs as smoothly as possible and is easily perceptible by routine measurements, we have found[1] that a sulfur vulcanizate of natural rubber tends to relax in an oxygen atomsphere at a constant rate, that is, according to a zero order reaction, provided the sample is exposed to elevated temperature in an atmosphere of pure nitrogen for a "pre-relaxation" period during which time the stress relaxes by a certain amount.

Since we are of the opinion that the above mentioned results can possibly be used in determining the "rate of aging" under the influence of oxygen, we continued our investigations. The goal was not so much to make a contribution to the theory of stress relaxation as it was to outline more accurately the experimental conditions under which the decrease of stress in an oxygen atmosphere follows a zero order course, as well as to expand the field of observation.

EXPERIMENTAL RESULTS AND DISCUSSION

Nine vulcanizates were used in the work. They were in the form of threads or thin strips, several being technical products while the others were prepared by us as follows:

1. Natural rubber vulcanized with 8% sulfur and 1% Vulkazit H.
2. Gray threads, technical product, composition not known.

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* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by W. D. Wolfe, from *Kautschuk und Gummi*, Vol. 11, WT 210 to 214, August 1958. One table of data has been omitted to save space.

3. Natural rubber vulcanized with 0.35% sulfur, 1.8% tetramethylthiuram monosulfide (TMTM), 0.9% tetramethylthiuram disulfide (TMTD); 7% silica.

4. Natural rubber, same vulcanizing agents as in 3; TiO_2 (no silica).

5. Natural rubber vulcanized with 2.96% TMTD with 5% zinc oxide, 5 hrs at 130° C.

6. Natural rubber vulcanized with 3.21% sulfur, 2.1% mercaptobenzothiazole (MBT), 1% zinc stearate and 4.1% zinc oxide, 2 hrs at 120° C.

7 and 8. Technical products, threads, composition unknown.

9. Natural rubber vulcanized with 0.32% sulfur, 2.08% (TMTM) with 10% zinc oxide, 2 hrs at 130° C.

Tobolsky and coworkers[3] probably were the first to gather fundamental experimental data from which may be derived the laws followed by stress relaxation. According to them, the change in relative tension should follow a first order relation; and Tobolsky has given a theoretical derivation for it.

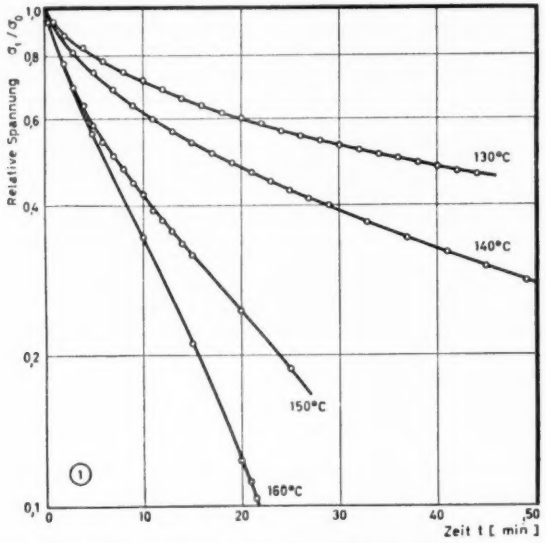


FIG. 1.—Decrease of relative stress with time in pure nitrogen at various temperatures and at 175% elongation (Vulcanizate 8). Ordinate: Relative tension σ_t/σ_0. Abscissa: Time, t (min).

However, since other workers have dealt with this problem, it has become evident that the relations are not nearly so simple as they seemed at first. Thus, Berry and Watson showed in the case of a sulfur vulcanizate that the curves for stress relaxation, in any case at earlier stages, did not satisfy a first order time law, either when measured in vacuum or in air. The curves satisfy a first order law only after the tension measured in air has decreased by about 50%[4]. On the other hand, the same authors found that peroxide vulcanizates, under sufficient oxygen pressure, do relax in accordance with a first order law. From these statements, it seems quite clear that the kinetics of tension relaxation are quite involved.

We show in Figure 1, for the case of Vulcanizate 8, that we do not get straight lines when the log of the relative tension measured in pure nitrogen is plotted against the time for relaxation; in other words, the tension relaxation does not follow a first order time law when measurements are made in pure

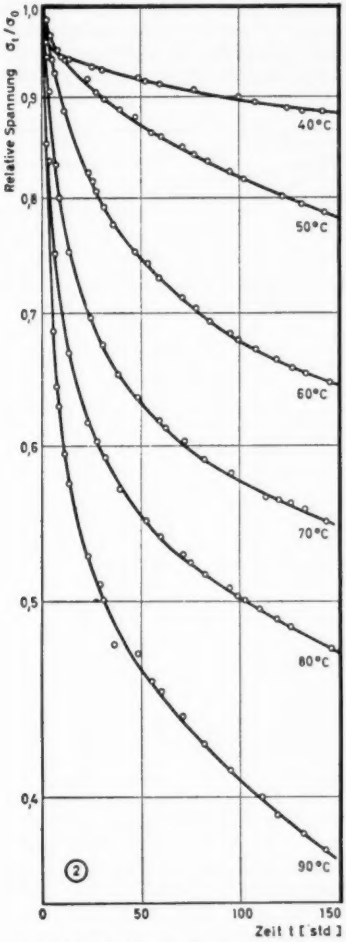


FIG. 2.—Decrease of relative stress with time in pure nitrogen at temperatures below 100° C and at 250% elongation (Vulcanizate 1). Ordinate: Relative tension (as in Figure 1). Abscissa: Time, t (hours).

nitrogen. The curves for 130° and 140° C are continuous arcs throughout the 50 minute time of observation. On the other hand, the curves for 150° and 160° C have an S shape, which, even if it is not very pronounced, can easily be seen.

Figure 2 for measurements made on Vulcanizate 1 in pure nitrogen and at lower temperatures (40° to 90° C) shows no different results; obedience to a first order law can certainly not be claimed for these conditions.

Also, when the measurements are made in air it is found that the tension relaxation does not obey a first order law. This is shown in Figure 3 in which the change in relative tension is plotted in a way which should show a first order variation. The curves for 50° and 60° C do not show very much because of the slight drop in stress (only about 20% in the 140 hour period), but it is evident that at least in their earlier course, they do not obey a first order law. But the

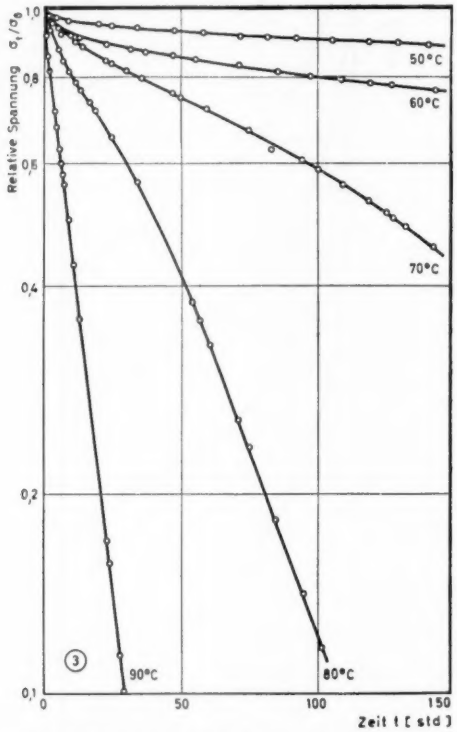


FIG. 3.—Change with time of relative tension plotted as a first order process at different temperatures in air at 250% elongation (Vulcanizate 1). Coordinates as for Figure 2.

curves for 70° and 80° C again show the S shape, which would possibly also show up at lower temperatures if the reduction in tension were followed in those cases to large enough values. Only the curve for 90° C can be considered as a straight line (agreeing with a first order relation). It would thus seem that the order of the reaction changes with the duration of the test period and furthermore that the results are dependent on temperature. The S shaped curves indicate deviations in direction toward an order that is higher than the first order

as well as toward one that is lower than first order. The preceding brings to mind the results of Berry and Watson[5] which showed changing reaction order for tension relaxation depending upon oxygen pressure. They found deviations from the first order in the direction of a higher order in the region of low oxygen pressure, compliance with the first order in the region of medium oxygen pressures, and deviations toward a lower order of reaction in the region of comparatively high oxygen pressures.

In Figure 4 we show the curves for stress relaxation in Vulcanizate 1 under oxygen, drawn to show first order behavior (Ordinate: log of the relative tension; Abscissa: relaxation time in hours). The results are fundamentally like those of Figure 3; the S shape of the curve is visible at 50° C, becomes quite apparent for 60°, 70° and 80° C, while the 90° C line indicates fair obedience to the first

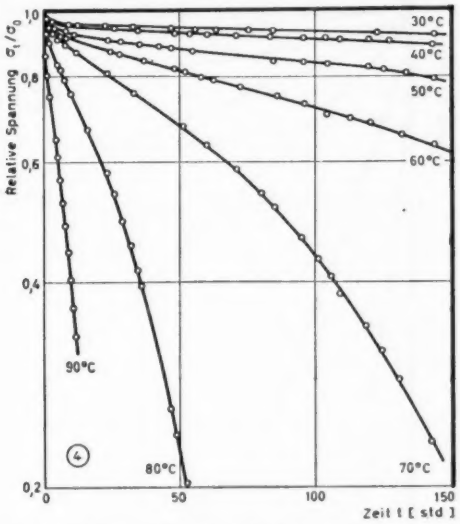


FIG. 4.—Change with time of relative tension plotted as a first order process at various temperatures in oxygen and at 250% elongation (Vulcanizate 1). Coordinates as for Figure 2.

order law. The decrease in tension at the lower temperatures is too slight for the period of time used, to make the course of the curves indicative.

It is clear from all these results that we are dealing with a complex process when we study stress relaxation; the difficulties are apparent when we try to determine and specify the reaction order. We are inclined to think that it is essential to do much more systematic investigating before writing any analysis or explanation of the phenomena. One thing is certain; stress relaxation cannot generally be considered as a first order process; it is evidently a first order process only under certain experimental conditions, which seem to change from case to case, and even then probably not over the whole range of the drop in tension.

In our opinion, certain very interesting applications for stress relaxation in practice are found when the variations of stress reduction are put on a plot to show zero order. This is done in Figure 5 for measurements on Vulcanizate 1

in oxygen. (Ordinate: relative stress; Abscissa: relaxation time in hours.) The deviation of the curves of Figure 4 in the direction of a course of lower order suggest this. With this method of plotting, it is shown that the lines, initially curved, soon go over into straight lines. This means that the decrease in relative tension follows a zero order course after a period of time of 10 to 20 hours, independent of temperature. Furthermore, the data follow this time law through a great portion of the experimental time period as well as of the decrease in tension. For instance, we find a linear relation between relative tension and time at 60° and 70° C throughout an experimental period of 130 hours! At temperatures below 50° C the evidence is vague because the decrease of tension is too slight.

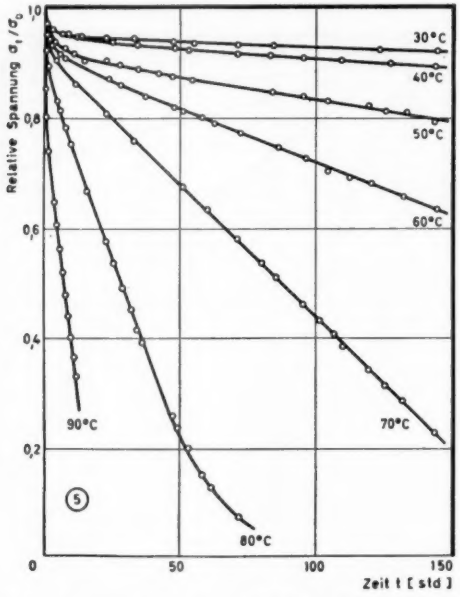


FIG. 5.—Change with time of relative tension plotted as a zero order process at various temperatures in oxygen and at 250% elongation (Vulcanizate 1). Coordinates as in Figure 2.

The relations which are shown by Figure 5 hold true for all the natural rubber sulfur vulcanizates. This led us to our previously published research work[1], the goal of which was to determine the conditions for measuring stress relaxation under which the process follows a zero order course from the very start; this also has the advantage that the difficulties connected with the determination of the initial tension are eliminated. We showed that the goal is attained when the vulcanizate is exposed to elevated temperatures for 4 or 5 days in pure nitrogen, for a period of "pre-relaxation". After such a preliminary treatment, the rate of reduction in relative tension of the material in oxygen follows the zero order course, so that an easy and convenient determination of its rate is assured in all cases.

It was soon found that it is desirable to specify the research conditions more exactly so that greater accuracy may be obtained in carrying out the measurements. The following experience (Paragraphs 1–6) was gained in the course of considerable research.

1) We have already[1] indicated—in agreement with the results obtained by Tobolsky[6]—that the rate of relaxation of tension in the zero order range is independent of elongation. In our measurements, the pre-relaxation and testing in oxygen were done at the same elongation. In the meantime we have found that it makes no difference what degree of elongation is used for pre-relaxation and measurements in oxygen; that is, the elongation may be chosen arbitrarily, but it should be at least 50%. We show this in Figure 6, where the temperature

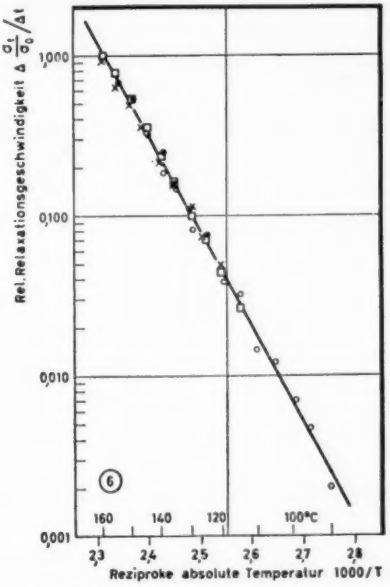


FIG. 6.—Dependence on temperature of the relative relaxation rate (pre-relaxation in pure nitrogen: 5 days at 90° C; relaxation rate measured in oxygen at 90° to 160° C) (Vulcanizate 3).

Elongation (%) during:	
Pre-relaxation	*Measurement in oxygen*
100	175
175	165
175	185
175	250

Ordinate: Relative relaxation rate. Abscissa: Reciprocal of absolute temperature, $1000/T$.

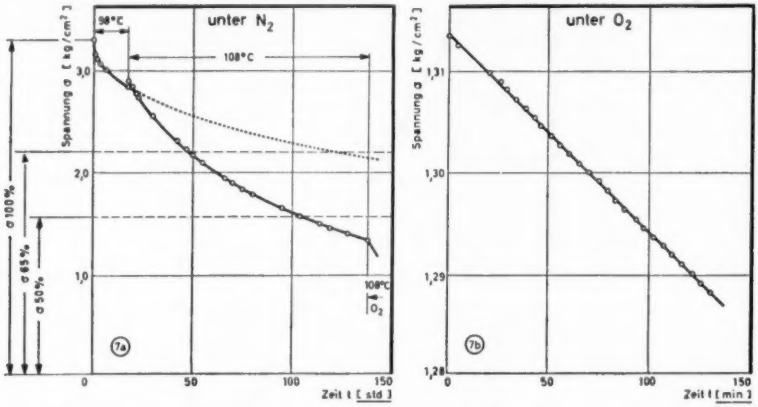
dependence of the relative relaxation rates is given in graphic form for Vulcanizate 3. The measurements made under widely different conditions of elongation for the pre-relaxation and the tests in oxygen all lie on a straight line with almost no deviation.

This does not hold for the relations in regard to the temperature at which the pre-relaxation and measurements in oxygen are performed, and with respect

to the magnitude of the drop in tension during the pre-relaxation. It was further shown:

2) During the pre-relaxation the stress should drop to about 60 or 50% of its starting value, otherwise the stress relaxation will not always follows a zero order time law at the start, and the curves will bend toward the ordinate. The time required to reach such a tension reduction naturally depends on the nature of the vulcanizate as well as upon the temperature at which the pre-relaxation takes place. A pre-relaxation period of 5 to 6 days is satisfactory when the following facts are considered.

3) The temperature above which the rate of change in relative tension, after a pre-relaxation period, always follows a zero order course, depends on the nature of the vulcanizate. This temperature is higher the more stable the vulcanizate; that is, the lower its relative rate of relaxation at a given temperature.



FIGS. 7a and 7b.—Determination of time and temperature as well as of minimum tension drop for the pre-relaxation (7a); course of the process as of zero order after pre-relaxation (7b) (Vulcanizate 9 at 80% elongation). Ordinate: Tension (kg/cm²). Abscissa: Time, *t*.

4) With vulcanizates of poor stability (high relative relaxation rates) the relaxation of tension in oxygen follows a zero order course when a pre-relaxation at temperatures above about 60° C is completed. This requires about 4 or 5 days. If these conditions are observed, then the stress relaxation follows the zero order with any elongation and for any temperature above 60° C.

5) With highly stable vulcanizates (very slow relaxation rates), the temperature for pre-relaxation should be 100° C or higher. Then the stress relaxation in oxygen, after a pre-relaxation of 4 to 5 days, will regularly run in a zero order course for every elongation and at temperatures above 100° C.

6) It is quite possible that the minimum temperature for the pre-relaxation may be further lowered but a longer time for the process would then have to be used, and extra precautions would be necessary. Below about 50° or 60° C, the method loses all certainty and becomes useless.

We show the relations prevailing in the pre-relaxation in Figure 7a. The stress is given there as a function of the pre-relaxation time. The temperature

at first was 98° C, for which the decrease in stress was followed during 20 hours. From the course of the curve (dotted line) it can be estimated that the material would still be under two-thirds of its initial tension after 125 hours (5 days). This is too much. Therefore the temperature was raised to 108° C. The steeply dropping curve now reaches the same drop in stress in 50 hours (2 days) and shows a decrease of 50% in 100 hours (4 days).

Now if the careful measurements in oxygen are started at about this time, or—as in the preceding examples—after 5 days (temperature being held constant and exact temperature measurements being made), the decrease will follow the zero order from then onward, as is shown in Figure 7b. The process was followed in this case for only two hours in oxygen, yet it would obey the law over a much wider interval (compare Figure 5). In this example, the temperature for pre-relaxation had to be about 100° C, because the material under study was a relatively stable (oxidation resistant) thiuram vulcanizate. We used Figures 7a and 7b to illustrate how we had to proceed in a practical case. In Figure 8 we give a group of zero order curves for relaxations at various

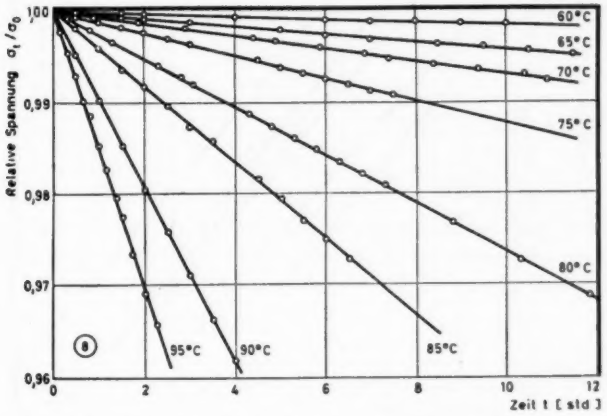


FIG. 8.—Course of stress relaxation of zero order in oxygen in conjunction with a pre-relaxation in pure nitrogen at 90° C and 100% elongation (Vulcanizate 2). Ordinate: Relative tension. Abscissa: Time, t (hours).

temperatures, such as are obtained with similar pre-relaxations. The experimental times here are longer than that given in Figure 7b.

The relative relaxation rates for Vulcanizates 1 to 8 are given in Figure 9. (Ordinate: log of relative relaxation rate; Abscissa: reciprocal of absolute temperature). The curves were obtained from all the linear functions described above. The individual points along the lines are average values of a number of measurements taken in oxygen with widely varying elongations.

As is shown in Figure 9, extraordinarily straight lines result from the use of the relations over a relatively wide temperature range; the Arrhenius law was followed[1] by Vulcanizate 1 over the range from 60° to 125° C. The temperature functions of the relative rates of relaxation of these various vulcanizates are here shown as practically parallel; this means that the degradation requires the same energy of activation in every case. We calculated the activation

energy for Vulcanizates 1, 2, 5, 6, 7 and 8 as 29.7 kcal/mole while the value for 3 and 4 was only a little less and was found to be 27.9 kcal/mole. From measurements thus far made, we would give an average value of about 29 kcal/mole, a value which is in good agreement with the value 30.4 kcal/mole which was given by Tobolsky and coworkers[7].

When we realize that oxygen can cleave sulfur crosslinks as well as main chain links and with the accompanying progressive breaking down of the molecular network during the drop in stress that rheological processes can possibly have part in the relaxation—this actually has given rise to all sorts of theoretical analyses and interpretations of tension relaxation[8]—it is really astonishing that the same activation energy is found in every case. This has led to the conception, that in spite of all the other possibilities, the oxidative degration of the

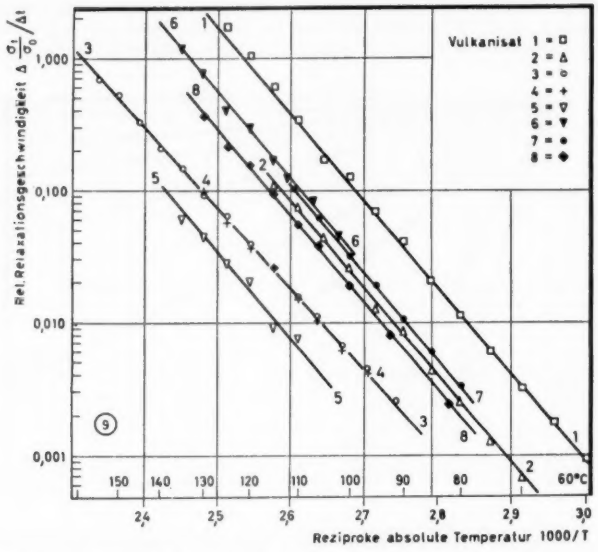


FIG. 9.—Temperature dependence of the relative relaxation rate in oxygen for Vulcanizates 1 to 8. Ordinate: Relative relaxation rate $\Delta \frac{\sigma_t}{\sigma_0}/\Delta t$. Abscissa: Recirpocal of absolute temperature, $1000/T$.

sulfur crosslinks must be the essential process in stress relaxation in sulfur vulcanizates. In our opinion this conception is confirmed by Figure 9; for in spite of the identical activation energies, the relative relaxation rates for the various vulcanizates are quite different (differences in the action constants), wherein the special constitution of the crosslinking shows up as it does in the extensive experimental work of Pedersen[9]. However, in past experience with identical activation energies, there is noted a variation in rates amounting at most to two powers of ten. This suggests stress relaxation as a basis for measurement of "aging rate" in oxygen. Notwithstanding the existence of a large amount of experimental data we would not make any detailed proposals until corresponding experiments have been made with loaded vulcanizates and until

it is found what happens when antioxidants are present. Stress relaxation is an unusually sensitive procedure; therefore we would hope that peculiarities which may be found in the kinetics of vulcanization reactions might be evident in the rate of tension relaxation. Therefore, the work will be continued along the lines indicated.

SUMMARY

The results of measurements of stress relaxation in natural rubber vulcanizates are reported. In the earlier work, the conditions were defined under which the drop in tension of a vulcanizate—after a pre-relaxation in pure nitrogen—follows a zero order law when tested in oxygen. The temperature dependence of the rate of relative tension relaxation was determined for 8 different vulcanizates. With a constant activation energy of about 29 kcal/mole, the vulcanizates differed in their relative relaxation rates at most by two powers of ten. Several general observations on the course of tension relaxation under different conditions were made on the grounds of experimental evidence. Good qualitative agreement was found with relations reported by Berry and Watson.

REFERENCES

[1] Scheele, W. and Hillmer, K-H., *Kautschuk u. Gummi* **9**, WT 82 (1956).
[2] Mochulsky, M. and Tobolsky, A. V., *Ind. Eng. Chem.* **40**, 2155 (1948).
[3] See Berry, J. P. and Treloar, R. L. G., in "Die Physik der Hochpolymeren", Band IV, Berlin, Heidelberg u. Göttingen, **1956**, p. 361 for related work by Tobolsky and coworkers as well as other authors.
[4] Berry, J. P. and Watson, W. F., *J. Polymer Sci.* **18**, 201 (1955).
[5] Berry, J. P. and Treloar, R. L. G., *loc. cit.*, 366, Figure V, 56.
[6] See Alfrey, T., "Mechanical Behavior of High Polymers", New York, 1948, p. 326. The work of Tobolsky is fully discussed in the section "Stress Relaxation in Vulcanized Rubber".
[7] Alfrey, T., *loc. cit.* 330; there also is reference to the original publications of Tobolsky.
[8] Theoretical considerations of stress relaxation are given by Berry, J. P. and Treloar, R. L. G., *loc. cit.*, p. 368. An explanation based on his own work is given briefly by Veith, A. G., *J. Polymer Sci.* **25**, 355 (1957).
[9] Pedersen, H. L., "Aging Properties of Low Sulfur Rubber Vulcanizates". Copenhagen, **1954**.

DIFFUSION PROCESSES IN THE VULCANIZATION OF TIRE STOCKS *

G. A. Blokh, Z. P. Kormilzeva, D. B. Boguslavskiĭ, B. I. Bakharev, and B. P. Tikhomirov

The use of radioactive isotopes has opened broad new possibilities for the study of diffusion across phase boundaries. Through the use of radioactive sulfur[1,2,3] any increased concentration of the vulcanizing groups has been determined in the boundary between phases (plies) of different sulfur containing structures and different articles such as insulation, varnish film and rubber footwear have been investigated.

In the present investigation an attempt was made to study diffusion during the vulcanization of tire stocks. For this purpose, radioactive sulfur (S^{35}) in place of ordinary sulfur was mixed into breaker, carcass and cushion compounds. Then, the diffusion of radioactive sulfur from one mixture into other rubber compounds was studied: from cushion stock to breaker and carcass; from breaker stock to cushion and carcass.

The rubber mixture containing radioactive sulfur (cushion, breaker or carcass) was extruded into a thin film (0.4–0.8 mm thick). From this film, 16 mm diameter discs were cut out. The discs were placed under a perpendicular counter and initial radioactivity measured from both sides of the sample before vulcanization. The discs were numbered and assembled into a sandwich 30 high in order to achieve the necessary thickness. The discs were insulated from each other by talc so that it was possible to separate them rapidly after vulcanization. Thus, the sandwich made of cushion stock containing S^{35} was assembled with nonradioactive breaker and carcass, using 8–10 discs

Table I

Diffusion of Radioactive Sulfur from Cushion into Breaker and Carcass

Radioactivity of cushion			Radioactivity after vulcanization			
			Breaker		Carcass	
Distance from nearest breaker layer, mm	Before vulcanization, counts per minute	After vulcanization, counts per minute	Distance from nearest cushion layer in mm	Counts per min	Distance from nearest breaker layer in mm	Counts per minute
0.00	1135	723	0.00	780	0.00	Background
0.65	1180	792	0.52	734	0.61	Background
1.50	1172	977	0.98	537	1.13	Background
2.41	1234	1132	1.53	405	1.70	Background
3.18	1173	1145	1.93	236	2.48	Background
4.16	1268	1220	2.54	125	3.05	Background
5.12	1240	1217	3.11	89	3.62	Background
5.98	1249	1240	3.56	46	4.30	Background

* Translated for Rubber Chemistry & Technology from *Kauchuk i Rezina* **17**, No. 7, 33–36 (1958).

TABLE II

DIFFUSION OF RADIOACTIVE SULFUR FROM THE BREAKER INTO CUSHION AND CARCASS

Initial radioactivity of breaker		Radioactivity after vulcanization			
		Cushion		Carcass	
Distance from nearest cushion layer, mm	Counts per minute	Distance from nearest breaker layer, mm	Counts per minute	Distance from nearest breaker layer, mm	Counts per minute
0.00	1433	0.00	1294	0.00	1317
0.69	1485	0.83	1062	0.39	1340
1.48	1292	1.60	554	0.91	973
2.21	1280	2.38	313	1.44	536
2.99	1581	3.21	171	1.98	312
3.69	1500	4.01	81	2.45	173
4.45	1410	4.83	54	2.93	99
4.83	1519	4.63	31	3.41	59

of the latter. In the same way the other radioactive sulfur containing mixtures were assembled with the other nonradioactive mixtures. In the first case, diffusion of S^{35} from cushion into breaker and carcass was studied; in the other two cases the corresponding movement of S^{35} was again followed. The assembly with S^{35} in the various layers was vulcanized at 145° for 0.5 to 2 hours. After vulcanization each disc which initially did not contain radioactive material was counted in order to establish the amount of radioactivity due to diffusion of S^{35}. That way not only the diffusion from one layer to the adjacent layer, but also the depth of penetration of the vulcanizing agent was determined. The results of these counts are given in Tables I–III.

From the data in Table I it is seen that the radioactive sulfur diffused from the cushion into the breaker to a depth of 3–3.5 mm. The highest concentration of the radioactive sulfur was found in the layer adjacent to the cushion at the depth of 0–0.5 mm. The activity of the breaker vulcanizate at 0.9 mm is more than 40% of the cushion activity at 1.5 mm and more than 60% of the cushion activity at 0.65 mm. However, the radioactive sulfur from the cushion did not penetrate into the carcass mixture. This is shown by the fact that the

TABLE III

DIFFUSION OF RADIOACTIVE SULFUR FROM CARCASS INTO BREAKER AND CUSHION

Initial radioactivity of carcass stock		Radioactivity after vulcanization			
		Breaker		Cushion	
Distance from nearest breaker layer, mm	Counts per minute	Distance from nearest carcass layer, mm	Counts per minute	Distance from nearest breaker layer, mm	Counts per minute
0.00	604	0.00	396	0.00	Background
0.65	626	0.56	374	0.62	Background
1.27	644	1.15	252	1.37	Background
1.94	640	1.72	153	2.04	Background
2.58	725	2.29	98	2.58	Background
3.26	704	2.83	68	3.52	Background

count of the carcass after vulcanization was equal to the background, i.e., no changes were observed in the discs due to radioactive sulfur diffusion from the cushion.

The following conclusions can be drawn from data given in Table II: during vulcanization radioactive sulfur diffused into the cushion as well as into the carcass; migrated radio sulfur was found at a depth of 3–4 mm; the highest radioactivity was found at a distance of 0–0.3 mm from the contact between breaker-carcass and breaker-cushion.

In contrast to the cushion, the breaker vulcanizate in a tire is known to perform under more complicated conditions since dynamic working properties of the breaker are determined by the bond strength between it and the cushion, and between it and the carcass, respectively.

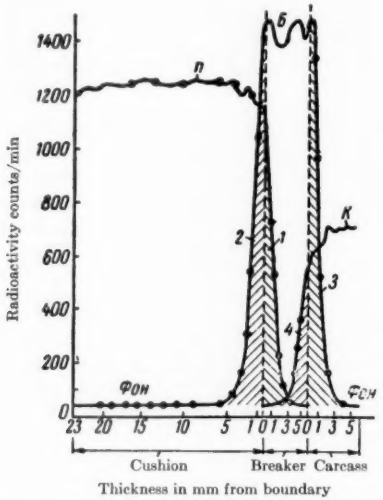


FIG. 1.—Schematic diagram of the distribution of radioactivity in the various tire stocks following vulcanization of sandwich constructions in which only one stock was initially radioactive. *n* is the level of initial radioactivity of cushion, *b* that of initially radioactive breaker and *K* that of the carcass. Curves *1* and *2* represent the activity of cushion-breaker boundary after cure and curves *3* and *4* that of the breaker-carcass boundary. Shaded areas are zones of increased concentration of S^{35}. ϕ_{OH} indicates the background activity.

From data given in Table III it may be concluded that the radioactive sulfur from the carcass mixture only penetrates into the bordering breaker layer. No S^{35} from the carcass was found in the cushion, i.e., radioactivity of the cushion layers bordering on the breaker was equal to that of the background. The radioactivity of the breaker rubber in layers bordering the carcass at the depth of 0.5–1 mm was 40–50% of the initial radioactivity of the carcass layers adjacent to the breaker.

In order to prove that through the vulcanization process an increased concentration of vulcanizing groups is formed in the boundary layers of different parts of a tire, radioactive cushion, breaker and carcass compounds were prepared and their initial count determined. Samples were pressed together and vulcanized at 145° for 2 hours. After vulcanization and separation of cushion

from breaker and carcass, the activity was determined in the boundary layers. The results of these tests are given in Table IV.

TABLE IV

RADIOACTIVITY OF BOUNDARY LAYERS OF TIRE STOCKS IN CONTACT

Bordering layer	Radioactivity, counts per min	
	Before vulcanization	After vulcanization
Cushion (to breaker)	993	1679
Breaker (to cushion)	1003	1493
Breaker (to carcass)	1208	1575
Carcass (to breaker)	508	1279

From a comparison of data given in Tables I–IV and the accompanying graph it becomes apparent that increased concentrations of vulcanizing groups are formed in the border layers where the breaker contacts cushion and carcass. This finding should be related to the kinetics of the chemical reactions of vulcanization within the separate stocks as well as in the boundary layers. Thus, bordering layers of breaker-with-cushion and breaker-with-carcass are zones of increased polysulfide concentration which undergo decomposition and regrouping during deformation of the tire. In the light of modern understanding of structure and fatigue of vulcanizates on deformation, the formation and decomposition of polysulfide linkages in the bordering layers has essential significance in the evaluation of the durability of the bonds in multiple articles[4,5].

Experiments involving diffusion of $Ca(OH)_2$ containing Ca^{45} from one tire stock to another during vulcanization showed that no diffusion occurred. This may be due to the fact that $Ca(OH)_2$ is insoluble in rubber and therefore diffusion can not take place.

CONCLUSIONS

1. The diffusion of radioactive S^{35} during vulcanization of rubber compounds used for tire building was investigated.

2. It was shown that during the vulcanization process an intense diffusion of the radiosulfur between plies can take place.

3. It was established that in the boundary layers "cushion-breaker" and "breaker-carcass" the concentration of the vulcanizing groups is increased; this may be the cause for different kinetics of the vulcanization reaction within any ply and at the boundary between plies. The increased concentration of vulcanizing groups should influence the spatial configuration of the boundary regions and the working qualities of polylayer articles.

REFERENCES

[1] Kargin, V. A. and Slonimskiĭ, G. L., *Doklady Akad. Nauk SSSR* **105**, 4, 751 (1955).
[2] Dogadkin, B. A., Collection "Prochnost svyazi mazhdu elementami rezino-tkanevykh mnogosloinykh isdeliĭ v proisvodstve i ekspluatatsiĭ", Goskhimizdat, 1956.
[3] Blokh, G. A., *Khim. Prom.* No. 2, 14–25 (1956).
[4] Blokh, G. A., "Sessia Akademiĭ Nauk USSR po mirnoum i spolsovaniyu atomnoi energiĭ.izd". *AN USSR*, Kiev (1956).
[5] Blokh, G. A., "IX conferencia po obshehim voprosam khimiĭ i fiziki visokomolecularnikh soyedineniĭ", *Izd. AN USSR* (1957).

THE INFLUENCE OF ACTIVATORS ON THE VULCANIZATION PROCESS. I. THE INFLUENCE OF ZINC OXIDE ON THE RATE OF COMBINATION OF SULFUR WITH RUBBER *

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The vulcanization of rubber is now carried out with sulfur, organic accelerators and vulcanization activators. Metallic oxides are used as activators, of which the most widely accepted is zinc oxide.

Most scientific workers have been and still are of the opinion that zinc oxide is an activator (promoter) for organic accelerators. This is the reason why all the theories which elucidate the mechanism of organic accelerators are more or less connected with reactions in which ZnO participates[1].

Elucidating the mechanism of the action of organic accelerators by studying zinc oxide was a result of the investigators' effort to explain this process by a single reaction. The starting point was taken as the following experimental determinations: during the process of vulcanization in the presence of zinc oxide zinc salts of the accelerators are formed; ZnS is formed; the addition of ZnO causes the vulcanizate to exhibit better mechanical properties. The vulcanization was considered as a single reaction (the combination of sulfur). Very little was known about the influence of individual rubber additives on the combination rate of sulfur, and on the mechanical properties of vulcanizates.

Lately some of the researchers[2] share the opinion that zinc oxide has more influence on the formation of spatial lattice structures in the vulcanizate than on the rate of sulfur combination. However, the opinions of investigators and their experimental results are frequently contradictory. Hence the influence of activators requires further investigation.

EXPERIMENTAL PART

The influence of ZnO on the kinetics of sulfur combination was traced in stocks of sodium-catalyzed polybutadiene rubber (SKB-35), which was obtained through polymerization in the gaseous phase with a paste catalyst having a 0.67% content of sodium (calculated as Na_2CO_3). The stocks were prepared on a laboratory mill and were vulcanized in an electric press at a temperature of 142° C.

The composition of the basic stock was: 100 SKB, 3 sulfur and 2 phenyl-2-naphthylamine (figures given in parts by weight). To this stock, as needed, further ingredients were added: zinc oxide, stearic acid and organic accelerators mercaptobenzothiazole (MBT) and diphenylguanidine (DPG).

In the vulcanizate the quantity of free sulfur and ZnS was determined iodometrically, and the quantity of combined sulfur after extraction with acetone

* Translated by Vera Doron and Malcolm Anderson from *Chemické Zvesti*, Vol. 12, 5, 304–311 (1958).

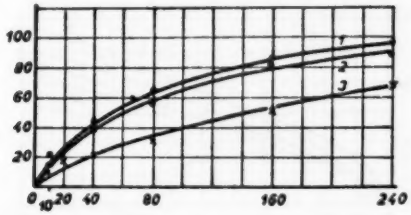


FIG. 1.—Kinetics of sulfur combination in stocks of SKB-30 without the addition of an accelerator. *1.* Basic stock. *2.* Stock B-2. *3.* Stock B-3. The abscissa represents vulcanization time in minutes, the ordinate the ratio of combined to total sulfur in per cent.

was determined gravimetrically by the oxidation of the samples with a mixture of nitric acid and bromine in the presence of magnesium oxide[3].

During the course of the work the influence of ZnO and of stearic acid were traced separately, as well as their combined influence on the kinetics of sulfur combination, and this was done in stocks prepared with industrial grade rubber as well as in stocks of rubber purified of their sodium content. The composition and designation of the stocks are given in Table I.

TABLE I

Name of ingredient	Designation						
	B-2	B-3	B-6	B-7	B-8	B-9	B-10
SKB	100[a]	100[a]	100	100	100	100	100
Sulfur	3	3	3	3	3	3	3
Zinc oxide	5	5	—	5	—	5	5
Stearic acid	2	—	—	2	—	5	5
PBNA	2	2	—	—	2	2	—

[a] SKB-30 with a sodium content of 0.56%. Numbers show parts by weight.

In Figures 1 and 2 the kinetics of sulfur combination is shown in stocks of industrial rubber (SKB-35) without accelerators. As is evident, the addition of zinc oxide sometimes causes some decrease in the amount of organically combined sulfur. (Organically combined sulfur is the amount of sulfur which is obtained by subtracting the inorganically combined sulfur in the form of ZnS from the total amount of combined sulfur.) The presence of zinc oxide and stearic acid at the same time causes a considerable decrease in the rate of combination of sulfur with rubber, and this both in the presence and in the absence of antioxidants.

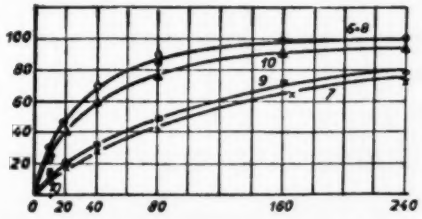


Fig. 2.—Kinetics of sulfur combination in stocks of SKB-35 without accelerator. *6.* Stock B-6. *7.* Stock B-7. *8.* Stock B-8 *9.* Stock B-9. *10.* Stock B-10 Further details as in Figure 1.

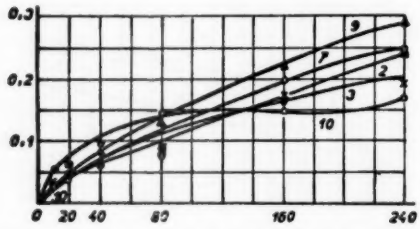


FIG. 3.—Kinetics of the formation of ZnS in stocks of SKB-30 and SKB-35. *2.* Stock B-2. *3.* Stock B-3. *7.* Stock B-7. *9.* Stock B-9. *10.* Stock B-10. The abscissa represents vulcanization time in minutes, the ordinate sulfur combined as ZnS in per cent.

We had shown earlier[4] that the decrease in the rate of sulfur combination with rubber is caused by a neutralization of the accelerating influence of the sodium compounds by stearic acid, by which sodium stearate is formed. PBNA (phenyl-2-naphthylamine) has practically no influence on the rate of sulfur combination, although it does have an influence on the formation of zinc

TABLE II

Name of ingredient	Designation							
	B-12	B-13	B-14	B-16	B-C[a]	B-D[a]	B-21	B-22
SKB-35	100	100	100	100	100	100	100	100
Sulfur	3	3	3	3	3	3	3	3
Zinc oxide	—	—	5	5	—	5	—	5
Stearic acid	—	2	2	—	—	2	—	2
MBT	1	1	1	1	1	1	—	—
DPG	—	—	—	—	—	—	1.2	1.2
PBNA	2	2	2	2	2	2	2	2

[a] SKB-35 purified from sodium compounds.

sulfide in the vulcanizate (see Figure 3). The largest amounts of zinc sulfide are formed in stocks which contain stearic acid and antioxidant.

The influence of activators on the kinetics of sulfur combination with rubber was traced in stocks containing accelerators. The composition and designation of some stocks are given in Table II.

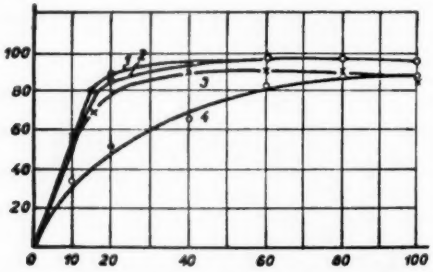


FIG. 4.—Kinetics of sulfur combination in stocks of SKB-35 with MBT. 1. Stock B-12. 2. Stock B-13. 3. Stock B-14. 4. Stock B-16. The abscissa represents vulcanization time in minutes, the ordinate the ratio of organically combined to total sulfur in per cent.

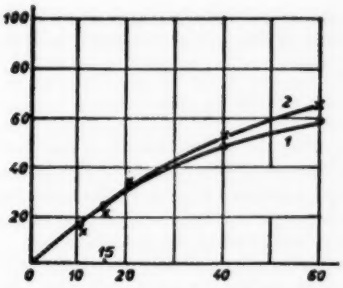


FIG. 5.—Kinetics of sulfur combination in stocks with SKB-35 purified of sodium. *1*. Stock B-C. *2*. Stock B-D. Further details as in Figure 4.

Figure 4 shows the course of vulcanization in a stock with mercaptobenzothiazole (MBT). As is evident, zinc oxide basically reduces the rate of sulfur combination with rubber; stearic acid has practically no influence on this rate. It has been shown earlier, however, that stearic acid reduces the rate of sulfur combination in stocks which do not contain accelerators, because of its neutralization of the accelerating influence of sodium compounds. Therefore, in stocks containing MBT, stearic acid must cause its activation, and with it also the acceleration of the combination of sulfur with rubber.

Thus stearic acid in stocks which contain MBT causes on the one hand a neutralization of the sodium compounds and an accompanying reduction in the rate; while on the other hand it causes the activation of MBT, which is followed by an increase in the rate; the resulting rate of sulfur combination with rubber, however, differs hardly at all from the rate with MBT itself (B-12). Therefore it is reasonable to expect that in stocks of rubber purified of sodium compounds, stearic acid should increase the rate of the sulfur combination with rubber. This hypothesis was also proven experimentally (see Figure 5); one must, however, emphasize that the accelerating action of stearic acid is really much more pronounced, since in the presence of zinc oxide, zinc sulfide is formed (approximately 8%) as well as zinc stearate, which results in a smaller amount of organically bound sulfur.

From Figure 6 it is evident that ZnO and stearic acid have no influence on

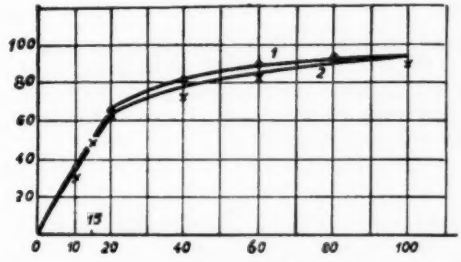


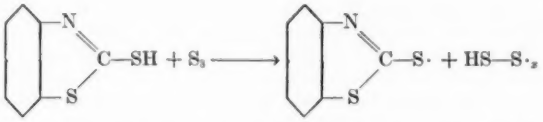
FIG. 6.—Kinetics of sulfur combination in stocks of SKB-35 with DPG. *1*. Stock B-21. *2*. Stock B-22. Further details as in Figure 4.

the rate of sulfur combination with rubber in stocks with DPG. From this it follows that the influence of zinc oxide and stearic acid is dependent on the type of organic accelerator used.

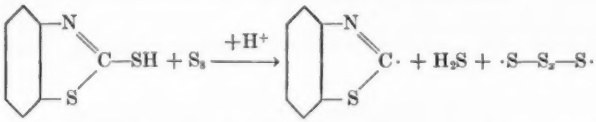
DISCUSSION

It is known that during the vulcanization of stocks containing MBT in the presence of ZnO a zinc mercaptide is formed. The latter is a less active accelerator than MBT itself, however. Therefore the reduction in the rate of sulfur combination is caused by the formation of zinc mercaptides. Its formation is the main process at the beginning of the vulcanization. Later on the zinc mercaptide decomposes from the effect of H_2S, and MBT is formed. In addition to the formation of zinc mercaptide, zinc sulfide is also formed in the system as a result of several reactions[4], resulting in a decrease in the amount of organically combined sulfur.

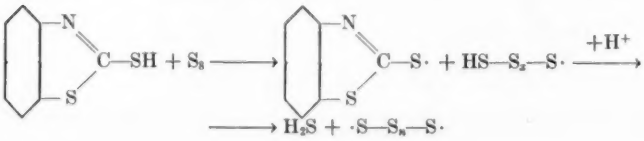
The activating influence of stearic acid has long been known from technological experience, although so far it has not been elucidated. When the isotope exchange between the sulfur of the SH group of MBT and elemental sulfur S^{35} was observed, it was found[4] that stearic acid increases the rate of this reaction considerably, and hence a reaction between MBT and stearic acid takes place. In the work of Dogadkin and Tutorskiĭ[5] it was also shown that stearic acid reacts with MBT with the subsequent formation of hydrogen sulfide. On the basis of these findings it is possible to explain the accelerating influence of stearic acid on the rate of sulfur combination with rubber in MBT stocks as follows: MBT during the process of vulcanization reacts with sulfur to form free radicals:



In the presence of stearic acid H_2S is formed, and therefore it is possible that the formation of free radicals follows a course as given below:



The formation of hydrogen sulfide by the above reaction, however, is linked with a scission of the C—S bond in MBT. The energy of this bond is greater (approximately 54 kcal/mole) than the energy of rupture of an eight-membered ring of S_8 (approximately 30 kcal/mole). Therefore free radicals and H_2S can be formed by the following reaction:



The formation of H_2S takes place also in the absence of sulfur. Therefore the scission of the C—S bond must occur; this is possible through the polarization of this bond by the presence of stearic acid. The accelerating influence of stearic acid thus lies in its activation of MBT through polarization. This conclusion agrees well with the opinion of G. A. Blokh[6] concerning the mechanism of the exchange reaction between elemental sulfur S^{35} and the sulfur of the SH group of MBT.

If zinc oxide and stearic acid are present at the same time in the rubber stock, two mutually competing reactions take place: the activation of MBT by stearic acid and the formation of a zinc mercaptide. The first reaction increases, and the latter decreases, the rate of sulfur combination. Sodium stearate and zinc stearate are formed, as well as zinc sulfide. Therefore the resulting influence of these reactions is manifested as a small decrease in the organically combined sulfur.

An analogous effect of zinc oxide and stearic acid upon MBT was also observed when the influence on the rate of the exchange reaction between elemental sulfur S^{35} and the sulfur of the SH group of MBT was observed[7].

SUMMARY

In this work the effect of zinc oxide and stearic acid on the kinetics of sulfur combination with rubber was traced, in stocks containing accelerators as well as in stocks without the latter.

It was proved that ZnO does not increase the rate of sulfur combination in sodium catalyzed polybutadiene rubbers (SKB-25). On the contrary, in stocks with mercaptobenzothiazole, zinc oxide decreases the rate of sulfur combination.

In vulcanizates ZnS is formed in the presence of ZnO. The largest amount of zinc sulfide is formed in stocks with phenyl-2-naphthylamine and with stearic acid.

REFERENCES

[1] Zeide, O. A. and Petrov, K. D., *Kauchuk i Rezina* **2**, 53 (1937); Auerbach, I., *Ind. Eng. Chem.* **45**, 1526 (1953); Petrov, K. D., *Zhur. Priklad. Khim.* **16**, 214 (1943); Bruni, G. and Romani, E., *India Rubber J.* **62**, 63 (1921); Bedford, C. and Sebrell, L., *Ind. Eng. Chem.* **13**, 1034 (1921).
[2] Olsen, S. R., Hull, C. M., and France, W. G., *Ind. Eng. Chem.* **38**, 1273 (1946); Hull, C. M., Weinland, L. A., Olsen, S. R. and France, W. G., RUBBER CHEM. & TECHNOL. **21**, 553 (1948).
[3] Beniska, J., Dissertation, Moscow, **1955**.
[4] Dogadkin, B. and Beniska, J., *Kolloid. Zhur.* **18**, 167 (1956).
[5] Dogadkin, B., Tutorskiĭ, I. and Pevzner, D., *Doklady Akad. Nauk SSSR* **112**, 449 (1957).
[6] Blokh, G. A., *Doklady Akad. Nauk SSSR* **91**, 1107 (1953).

THE INFLUENCE OF ACTIVATORS ON THE VULCANIZATION PROCESS. II. THE INFLUENCE OF ZINC OXIDE ON THE STRUCTURE OF VULCANIZATES *

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During the process of vulcanization a single spatial structure is formed in which the individual molecules of rubber are linked together by two kinds of bonds: bonds of intermolecular attraction, and chemical bonds of different energies[1]. The ratio, concentration and energy of these bonds determine the physicochemical and mechanical properties of vulcanizates.

Individual rubber additives exhibit different influences on the final product. From technological experience it has been known for a long time that zinc oxide improves the mechanical properties of the vulcanizate, but only very recently is its influence being explained in connection with structural changes within the vulcanizate[2].

EXPERIMENTAL PART

The influence of zinc oxide on the structure of vulcanizates was traced by way of kinetic swelling results by the method of determining equilibrium swelling (maximum swelling, Q_m). Tracing the formation of crosslinks ($\gamma/2$) between rubber molecules during vulcanization by the method of swelling is a rapid and highly reproducible procedure. The molecular weight of a fraction of the molecular chain M_c was calculated from the values of swelling Q_m which are presented in Figure 1, and the number of crosslinks ($\gamma/2$) according to the

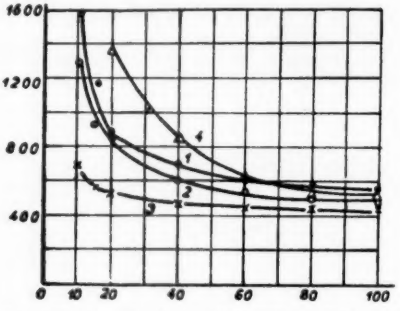


Fig. 1.—Kinetics of the swelling of vulcanizates with MBT. *1.* Basic stock: 100 parts SKB (polybutadiene) by weight, 3 parts sulfur, 2 parts PBNA. *2.* Basic stock + 2 parts stearic acid. *3.* Basic stock + 5 parts ZnO + 2 parts stearic acid. *4.* Basic stock + 5 parts ZnO. The abscissa represents vulcanization time in minutes, the ordinate Q_m in per cent by volume.

* Translated by Vera Doron and Malcolm Anderson from *Chemické Zvesti*, Vol. 12, 6, 376–381 (1958).

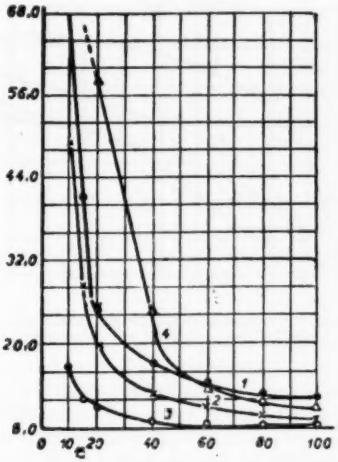


FIG. 2.—Change in the molecular weight of chain fractions of molecules (M_c) during the course of vulcanization. The abscissa represents time of vulcanization in minutes, the ordinate $M_c \times 10^{-3}$. Stock composition as in Fig. 1.

equation of Flory and Rehner[3]. The calculated values are given in Figures 3 and 4. As is evident from Figure 2, and even more from Figure 3, ZnO alone, in stocks with mercaptobenzothiazole (MBT), causes practically no increase in the number of crosslinks; on the contrary, at the beginning of the vulcanization process it reduces the rate of crosslinking of chains, which is revealed in a reversion of the vulcanizate after a 10-minute vulcanization period (the composition and labeling of the stock is given in the previous work[4]). When the process of vulcanization continues further, the rate of formation of crosslinks increases in such a way that at the end of the vulcanization process the degree of crosslinking in the vulcanizate is the same as in the vulcanizate which did not contain zinc oxide. Stearic acid has little influence on crosslinking. The maximum rate of crosslinking as well as the maximum number of crosslinks is achieved by the simultaneous presence of ZnO and stearic acid in the stock (Curve *3* of Figures 1 and 3).

Thus zinc oxide exhibits its influence fully only in the presence of stearic acid by way of zinc stearate formation, the stearate being more soluble in rubber than ZnO.

The influence of zinc oxide on the formation of a spatial structure is still more evident from Figure 4. The number of crosslinks increases with the amount of organically combined sulfur in all stocks, but this increase is most pronounced in a stock containing ZnO and stearic acid (Curve *3*). For example, with an equal quantity of organically combined sulfur (8 gram atoms of sulfur per g of stock) this increase is as much as three-fold. An equal quantity of organically combined sulfur thus can form a variable yield of crosslinks, depending on the presence of activators of the vulcanization process.

From Figure 4 it is further evident that not a single curve passes through the origin, but transects a certain segment of the abscissa. This segment is the smallest in the case of Curve *3*, which corresponds to the stock containing zinc

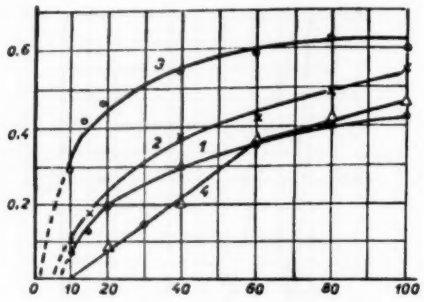


FIG. 3.—Kinetics of crosslinking. The abscissa represents vulcanization time in minutes, the ordinate the crosslinks (moles $\times 10^4$/gram of stock). Further details as in Fig. 1.

oxide and stearic acid. From this it follows that a single spatial structure of the vulcanizate is formed only after a certain quantity of sulfur has already combined with the rubber. This quantity of sulfur is smaller in the case of a stock with ZnO and stearic acid than in a stock without activators. This may possibly be explained by either the fact that in this case less sulfur is combined intramolecularly, or that one crosslink sulfur bond (sulfur bridge) contains a smaller number of sulfur atoms. In both cases, however, the sulfur is used more economically in the presence of activators, in the process of forming a single spatial structure in the vulcanizate. Therefore the influence of zinc oxide during the process of the vulcanization of stocks with MBT lies in its activation of crosslinking, i.e., in the activation of the formation of a spatial structure in the vulcanizate, and thus also in the improvement of its physico-mechanical properties.

There is a linear correlation between the number of crosslinks and the organically combined sulfur. This relation is disturbed, however, when practically all the sulfur has combined with the rubber. The formation of new crosslinks, when the vulcanizate contains no more free sulfur (the almost vertical parts of the curves in Figure 4), indicates that these arise from the polysulfide bonds which had been formed in the beginning steps of the vulcanization process.

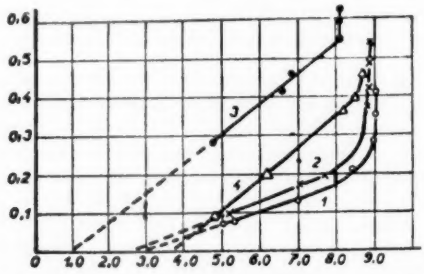


FIG. 4.—Formation of crosslinks as a function of the quantity of combined sulfur. The abscissa represents organically combined sulfur (gram-atoms $\times 10^4$/gram of stock), the ordinate the amount of crosslinks (moles $\times 10^4$/gram of stock). Further details as in Fig. 1.

DISCUSSION

On the basis of the experimental results one may state that the formation of a spatial structure in the vulcanizate is a result of several chemical reactions. There is first of all the direct combination of molecules of rubber through sulfur biradicals, which results mainly in the formation of polysulfide bonds. The biradicals of sulfur are formed through the mutual interaction of the organic accelerator, sulfur and rubber:

$$RH + S_8 \rightarrow R\cdot + HS_x\text{—}S\cdot \rightarrow HS\cdot + \cdot S\text{—}S_{x-1}\text{—}S\cdot$$

where RH is either an accelerator or a rubber molecule.

The HS· or HS_xS· radical can combine with the double bonds of rubber molecules, or they can react with sulfur, thus forming rubber mercaptans, i.e., thiol radicals. The combination of these latter with the rubber molecule is not followed by the immediate formation of crosslinks, but on the contrary, is followed by the formation of intramolecular cyclic bonds. Therefore in stocks containing MBT only, only a few crosslinked bonds are formed (Curve *1* of Figure 4), since in this case a large amount of H_2S is also formed as a result of the reaction between MBT, sulfur and stearic acid. The zinc oxide present in the stocks reacts with hydrogen sulfide. This reaction takes place even more rapidly in the presence of stearic acid, because zinc stearate is formed. Therefore in stocks with zinc oxide and stearic acid more crosslinks are formed.

Crosslinks can form also by the oxidation of the rubber mercaptans. According to the opinion of various authors the oxidation may be caused either by sulfur[5] or by zinc oxide[6]. Bloomfield[7] states that ZnO catalyzes the oxidation of mercaptans by sulfur; amines can have a similar effect. Most of these authors agree that during the oxidation process H_2S is formed, though they deny that it reacts with ZnO to give ZnS. Other authors[8] are of the opinion that the role of zinc compounds during vulcanization is to maintain the optimum "level" of H_2S, which when present in small quantities catalyzes, though in large quantities it inhibits, the vulcanization process. On the basis of these opinions and of our experimental data[9] it is possible to illustrate the formation of crosslinks by the oxidation of rubber mercaptans schematically as follows:

$$\begin{matrix} R_1\text{—}SH \\ R_2\text{—}SH \end{matrix} + \cdot S\cdot_x \xrightarrow{+\,Zn^{++}} \begin{matrix} R_1 \\ | \\ S \\ | \\ S \\ | \\ R_2 \end{matrix} + ZnS + \cdot S\cdot_{x-1} + 2H^+$$

where R_1 and R_2 are rubber molecules.

Finally, crosslinks are also formed by the decomposition of the polysulfide bonds which were formed by the direct combination of rubber molecules with sulfur biradicals or by the oxidation of the thiol groups in the rubber. Sulfur bonds thus formed contain a smaller amount of sulfur atoms per crosslink. This process of formation of new crosslinks goes on throughout the entire process of vulcanization, though it predominates toward the end of the vulcanization, when all the sulfur has already been bound to the rubber (the vertical parts of the curves in Figure 4). This is especially evident in stocks without zinc oxide. In stocks which do not contain ZnO, therefore, more polysulfide bonds are formed, but less monosulfide and disulfide bonds, and therefore also

more new crosslinks, which are formed by the decomposition of the already existing polysulfide bonds. We became convinced of this through experiments with vulcanizates without zinc oxide, which were heated for 8–10 hours in an atmosphere of nitrogen at a temperature of 126° C. The maximum swelling Q_m before the heating was 5.94, after the heating 5.1 and 5.2. On the other hand, the Q_m value of vulcanizates with zinc oxide increased, thus confirming its partial conversion. In a previous work[10] we have proved that this occurrence is related to the formation of ZnS. We shall deal with this problem in detail later on.

SUMMARY

The influence of zinc oxide and stearic acid on the structures of vulcanizates was traced in stocks with mercaptobenzothiazole by means of the kinetics of swelling.

It was found that zinc oxide in the presence of stearic acid has a marked influence on the rate and degree of crosslinked network formation in vulcanizates. In the formation of crosslinks (sulfur bridges) a number of reactions participate: the direct combination of rubber molecules with biradicals of sulfur, during which polysulfide bonds are mainly formed; the oxidation of rubber mercaptans (–SH groups), which is followed by the formation of monosulfide, disulfide and polysulfide links; and the decomposition of polysulfide links, which is followed by the formation of new crosslinks with a smaller number of sulfur atoms per crosslink.

Zinc oxide has a varying influence on the individual reactions: the first two are activated by it, and the last one is retarded by it, because it does not react with the polysulfide sulfur to form zinc sulfide.

REFERENCES

[1] Dogadkin, B. A. and Tarasova, Z. N., *Doklady Akad. Nauk SSSR* **85**, 1069 (1952).
[2] Adams, H. E. and Johnson, B. L., *Ind. Eng. Chem.* **45**, 1539 (1953).
[3] Flory, P. and Rehner, J., Jr., *J. Chem. Phys.* **11**, 52 (1943).
[4] Beniska, J. and Dogadkin, B., *Chem. Zvesti* **12**, 304 (1958); preceding paper, this issue.
[5] Fisher, H. L., *Ind. Eng. Chem.* **31**, 1381 (1939).
[6] Barton, B. C. and Hart, E. J., Rubber Chem. & Technol. **26**, 510 (1953).
[7] Bloomfield, G. F., Rubber Chem. & Technol. **21**, 543 (1948); *J. Polymer Sci.* **1**, 312 (1946).
[8] Craig, D., Juve, A. E., Davidson, W. L., Semon, W. L. and Hay, D. C., *J. Polymer Sci.* **8**, 321 (1952).
[9] Beniska, J., Dissertation, Moscow, 1955.
[10] Dogadkin B. and Beniska, J., *Kolloid. Zhur.* **18**, 167 (1956); Beniska, J. and Dogadkin, B., *Chem. Zvesti* **12**, 304 (1958); preceding paper, this issue.

THE STRUCTURE AND PROPERTIES OF RUBBERS PRODUCED IN RADIATION VULCANIZATION *

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In recent years there have been great advances in studies of the action of high-energy radiations on various substances and processes. In particular, there has been great interest in the utilization of nuclear radiations for the vulcanization of polymers[1–4]. The reason for this interest is that, according to the available literature data, vulcanizates obtained under the influence of ionizing radiations have structural characteristics which distinguish them from ordinary products obtained by chemical vulcanization. According to Jackson and others[2], irradiation vulcanizates have high resistance to thermal and thermo-oxidative aging, to the action of solvents and softeners at high temperatures, and to the action of chemically active media.

The method of vulcanization with the aid of ionizing radiations also differs from the ordinary thermochemical methods in a number of respects; the vulcanization can be effected without the use of heat or vulcanization agents. Ionizing radiations can bring about the vulcanization of saturated polymers which cannot be vulcanized by any other known methods. The interest in the vulcanization of such chemically inert polymers is due to their high resistance to various forms of aging and corrosive media. One advantage of irradiation vulcanization is the possibility of the production of homogeneous massive articles, owing to the high penetration of the radiation. All the processing steps can be accelerated because vulcanization agents which may cause premature vulcanization (scorching) are not used. The vulcanization time can also be shortened by the use of powerful sources of radiation, since the degree of crosslinking is determined by the integral dose of radiation absorbed.

The object of the present investigation was a study of the structural characteristics of irradiation vulcanizates and their physicochemical and technical properties, and the development of formulations and technological procedures in the use of ionizing radiations in technical vulcanization.

Irradiation vulcanization was effected in a nuclear reactor and in a Co^{60} unit of 20,000 curie power. The integral dose of the absorbed energy was in the range 10^7–10^8 roentgen; the dose rate was between 1.36 and $0.43 \cdot 10^6$ r/hour. During the cobalt irradiation the temperature of the specimens did not rise above that of the room. Special determinations of the temperature in the specimens in the reactor were not carried out. The temperature was probably 100–150° in the stated dose range. The irradiation vulcanizates made in the nuclear reactor had residual radioactivity. These specimens were tested 2–3 weeks after preparation; the residual radioactivity decreased to near the background level during this period.

* Reprinted from Colloid Journal **20**, pages 248–258 (1958); a translation by Consultants Bureau, Inc. of *Kolloidnyi Zhurnal* **20**, 260–271 (1958).

THE IRRADIATION VULCANIZATION OF RUBBER

The irradiation vulcanization of purified and technical specimens of natural (NR), butadiene–styrene (SKS-30A), isoprene (SKI), and sodium butadiene (SKB) rubbers was studied.

Films 0.1–2.0 mm thick were made on cellophane from the sol fractions of solutions of the above-named rubbers in benzene. After evaporation of the benzene, the films on their cellophane supports were placed in aluminum cases of a standard type for vulcanization in the nuclear reactor, or in glass test tubes for irradiation with Co^{60}. The cases were always put into the same tube of the reactor to the same depth, at a given constant power of the reactor.

When the irradiation vulcanization was performed in oxygen-free conditions, the rubbers were first purified by extraction in acetone and reprecipitation from benzene solutions in a nitrogen atmosphere. The films were formed on cellophane and dried also in a nitrogen atmosphere, then placed in glass bulbs, repeatedly evacuated at 10^{-4} mm Hg, and the tubes were sealed under vacuum. The density of the vulcanization network in the irradiation vulcanizates was estimated from the maximum swelling in xylene (see Table I) and from the

TABLE I

MAXIMUM SWELLING IN XYLENE, OF TECHNICAL RUBBERS AFTER IRRADIATION VULCANIZATION IN PRESENCE OF AIR IN A NUCLEAR REACTOR

Composition of mixture	Maximum swelling in xylene, %	Composition of mixture	Maximum swelling in xylene
Integral radiation dose $38 \cdot 10^6$ r		Integral radiation dose $50 \cdot 10^6$ r	
SKS-30A + 40 wt. parts channel black	314		
SKS-30AM + 40 wt. parts channel black	321	Smoked sheet	362
NR + 40 wt. parts channel black	353	SKS-30A	432
		SKB	260
		SKI	754
NR + 40 wt. parts furnace black	369		
SKS-30A + 40 wt. parts furnace black	329		
SKS-30AM + 40 wt. parts furnace black	348		

value of the modulus determined at 60% deformation at 130°. Under these conditions the modulus approached the equilibrium value.

According to Table I, the technical rubbers form the following series in order of effectiveness of formation of a vulcanization network during irradiation vulcanization: SKB > NR > SKS-30A > SKI. This order may vary according to the initial weight, degree of purification of the rubber, nature of the medium, etc. In fact, the degree of crosslinking of purified butadiene–styrene rubber not containing phenyl-2-naphthylamine was considerably higher than that of purified natural rubber.

The presence of oxygen plays a very important part in crosslinking during irradiation vulcanization. For both the rubbers studied—natural and butadiene–styrene (SKS-30A)—the degree of crosslinking estimated from the maximum swelling and modulus at 130° is greater after irradiation in air than in vacuum, even in purified rubbers (Figures 1 and 2, and Table II). It is interesting to note the considerably lower degree of crosslinking in technical SKS-30A containing phenyl-2-naphthylamine, in comparison with rubber purified by extraction (Figure 2).

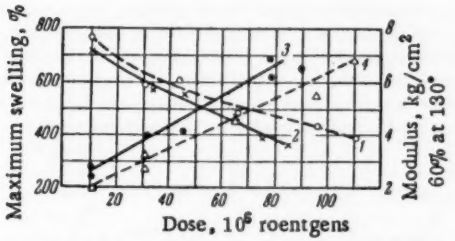


FIG. 1.—Influence of the medium during irradiation on the degree of crosslinking of purified natural rubber during irradiation vulcanization in a Co^{60} source: 1 and 2) Maximum swelling in xylene, %; 3 and 4) 60% modulus at 130°, in kg/cm²; 1, 4) In vacuum; 2, 3) In air.

The following results were obtained in studies of the infrared absorption spectra of purified and technical SKS-30A irradiated in a Co^{60} source in presence of air. The spectrum of purified SKS-30A contains strong bands of oxygen-containing groups after irradiation with a dose of $36 \cdot 10^6$ r (Figure 3, a). In

TABLE II

INFLUENCE OF THE MEDIUM DURING IRRADIATION VULCANIZATION OF RUBBERS IN A Co^{60} SOURCE

Rubber	Irradiation dose, roentgens $\times 10^{-6}$	Cross links per 100 ev during irradiation	
		In air	In vacuum
SKS-30A, technical	15	1.27	—
	30	2.24	—
	60	2.57	—
	90	2.62	—
SKS-30A, extracted	15	12.2	9.0
	30	9.0	6.0
	60	12.3	5.14
	90	15.5	4.97
NR, extracted	15	6.87	6.2
	30	3.89	4.0
	60	3.89	2.92
	90	4.37	2.82

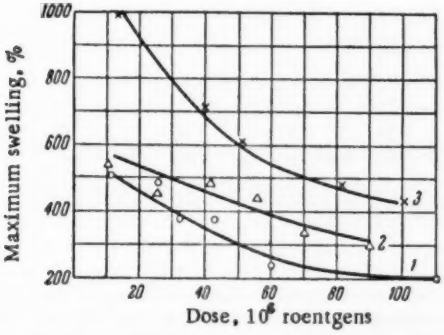


FIG. 2.—Influence of the medium during irradiation vulcanization of SKS-30A in a Co^{60} source: 1) Purified SKS-30A in air; 2) Ditto, in vacuum; 3) Technical SKS-30A in air.

the 5.8 μ region a broad absorption band appears, corresponding to carbonyl groups of acids, aldehydes, and ketones; in the 2.8 μ region, the absorption band of the hydroxyl group appears; the considerable decrease in transmission in the long-wave region of the spectrum between 7 and 11 μ indicates the appearance of ester (8–9.0 μ region) and ether (7.5–8 μ and 8.7–9.4 μ regions) groups. The band for alcohol hydroxyls is also in this last region.

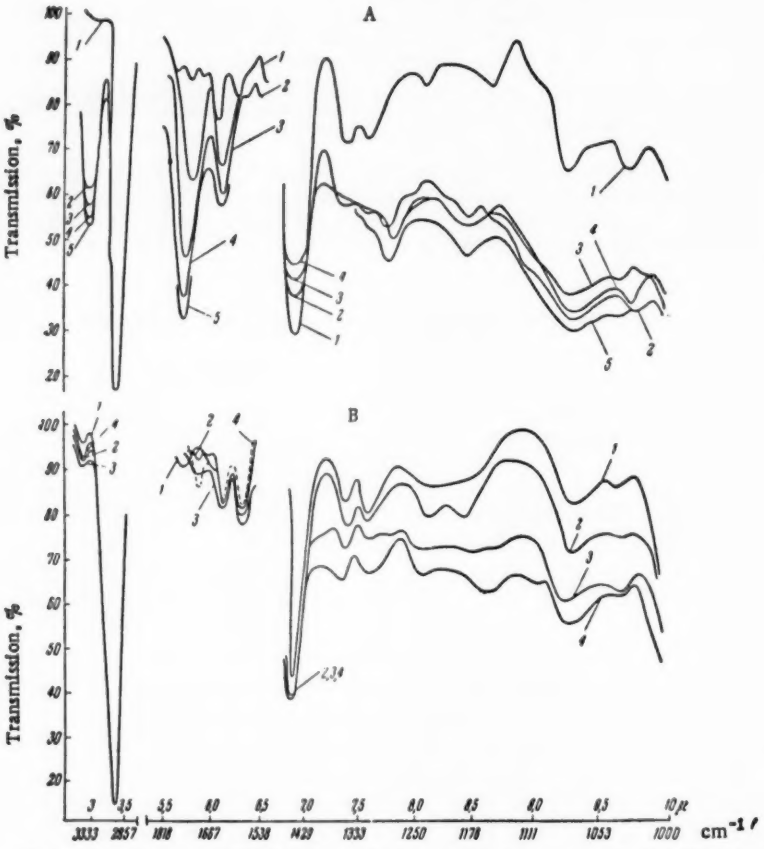


FIG. 3.—Infrared spectra of SKS-30A after irradiation in air in a Co^{60} source: A) Purified SKS-30A; B) SKS-30A with phenyl-2-naphthylamine; *1*) Raw rubber; *2*) After irradiation with $36 \cdot 10^6$ r; *3*) Ditto, $63 \cdot 10^6$ r; *4*) Ditto, $93 \cdot 10^6$ r; *5*) Ditto, $123 \cdot 10^6$ r.

With increase of the irradiation dose up to 10^8 r the absorption bands of the carbonyl groups become stronger and are displaced in the direction of shorter wave lengths, indicating the appearance of ester carbonyl groups. At the same time, on a background of decreasing transmission in the long-wave region, a band appears at 8.5 μ, corresponding to vibrations in the C—O—C groups of

esters. The intensity of the hydroxyl group absorption band also increases with increasing radiation dose.

Quantitative estimation of changes in the unsaturation of the purified specimens is difficult owing to the decreased transmission in the long-wave region of the spectrum. For quantitative estimation of the unsaturation from the strength of the absorption bands at 10.3 μ and 11.0 μ, all the spectra were raised to coincide at the transmission maximum (Figure 4). With this arrangement it is clear from Figure 4 that irradiation with a dose of $36 \cdot 10^6$ r the unsaturation decreases sharply both at the 1–4 and the 1–2 groups. When the dose is increased to $63 \cdot 10^6$ r, the unsaturation disappears almost entirely. When the dose reaches $\sim 10^8$ r, the number of double bonds in 1–4 groups increases again.

Comparison of data on the number of crosslinks (Table II) formed during irradiation, with the loss of double bonds shows that the decrease of unsaturation cannot be attributed only to polymerization crosslinking processes. The excess loss of double bonds is evidently the result of formation of intramolecular

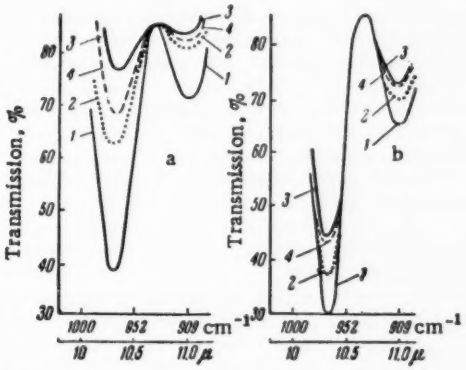


Fig. 4.—Variation of the unsaturation of SKS-30A during irradiation in a Co^{60} source in air. a) Purified SKS-30A; b) SKS-30A with phenyl-2-naphthylamine: *1*) Raw rubber; *2*) After irradiation with $36 \cdot 10^6$ r; *3*) Ditto, $63 \cdot 10^6$ r; *4*) Ditto, $93 \cdot 10^6$ r.

rings. These structural changes are one of the causes of the thermal resistance of irradiation vulcanizates.

The changes in the infrared absorption spectra of nonextracted technical SKS-30A (containing phenyl-2-naphthylamine) during irradiation are substantially different (Figure 3, b).

The spectrum of the original technical rubber already shows the presence of a small number of oxygen-containing groups. This is indicated by the presence of a weak hydroxyl group absorption band in the 2.9 μ region, and traces of carbonyl groups in the 5.9 μ region (Figure 3, b). When technical SKS-30A is irradiated with doses of $36 \cdot 10^6$ r and over, up to 10^8 r, there is a very slight increase in the intensity of these absorption bands, with a somewhat more pronounced decrease of transmission in the long-wave region.

The decrease of unsaturation as the result of irradiation is considerably less pronounced in nonextracted SKS-30A (Figure 4, b) than in the purified rubber. After irradiation with $60 \cdot 10^6$ r the number of double bonds in the 1–4 groups

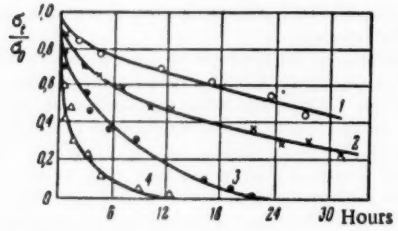


FIG. 5.—Stress relaxation of rubbers (at 130°, ϵ=60%, in nitrogen) subjected to irradiation vulcanization in air in a nuclear reactor, dose $50 \cdot 10^6$ r: 1) NR irradiation vulcanizate; 2) NR with thiuram without sulfur; 3) SKS-30A irradiation vulcanizate; 4) SKS-30A with sulfenamide and sulfur.

decreases by about 30% of the original content; the content of 1–2 type double bonds remains almost unchanged (Figure 4, b). The data on changes of unsaturation must be regarded as approximate because SKS-30A rubber contains styrene groups, which also give absorption bands at 10.3 and 11.0 μ, and the results of the unsaturation determinations are therefore somewhat distorted.

Comparison of the infrared spectroscopic data with the results of crosslink determinations indicates that the increased crosslinking in presence of oxygen is associated to some extent with formation of crosslinks of the ether type.

The protective role of phenyl-2-naphthylamine in irradiation vulcanization is apparently associated with scattering of the absorbed energy and with suppression of oxidative crosslinking.

The nature of the vulcanization bonds in irradiation vulcanizates was determined by a method developed previously[5], in which the rate of stress relaxation is measured at constant deformation at 130° in absence of oxygen. It was shown that under these conditions the relaxation rate is determined by the energy of the vulcanization bonds.

Figure 5 shows that the irradiation vulcanizate of natural rubber is superior in thermomechanical resistance to sulfurless vulcanizates with thiuram. The irradiation vulcanizates attain lower residual deformations and lower swelling maxima during relaxation under the conditions described than do the sulfur vulcanizates (Table III). The results show that the crosslinks formed in irradiation vulcanization are more resistant to heat than the crosslinks in sulfur vulcanizates.

Figure 6 shows the variation of the relaxation rate constant in irradiation NR vulcanizates with the number of crosslinks per unit volume, determined

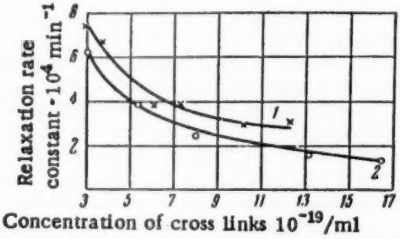


FIG. 6.—Variation of the stress-relaxation rate constant with the density of the vulcanization network in irradiation vulcanizates of purified natural rubber, obtained: *1*) In vacuum; *2*) In air.

TABLE III

CHANGES IN THE PROPERTIES OF NATURAL RUBBER VULCANIZATES DURING RELAXATION OF STRESS IN A NITROGEN ATMOSPHERE AT 130°

Vulcanizates	Maximum swelling in xylene, %			Residual elongation, %
	Initial Q_0	After relaxation Q_t	$\frac{\Delta Q}{Q_0}$	
NR with thiuram, without sulfur	447	765	+70	43.0
NR, integral dose $50 \cdot 10^6$ r	331	344	+ 4	6.7

from the maximum swelling in xylene. It is seen that the relaxation rate constant decreases with increasing density of the network. This is an important difference between irradiation and sulfur vulcanizates; for the latter it was shown[5] that the rate of relative relaxation of stress in not very hard vulcanizates does not depend on the number of crosslinks. The probable reason for the difference is a difference in the type of crosslinks. Whereas in the case of sulfur vulcanizates stress relaxation is the result of breakdown at branch points, in irradiation vulcanizates, which contain C—C crosslinks of higher stability than the diallyl bonds in the molecular chains, breakdown of the vulcanization network during chemical relaxation may occur not only at the branch points, but along the chains. In the latter case the rate of stress relaxation is inversely proportional to the number of branch points per unit volume of the vulcanizate[6].

It must also be noted that the relaxation curves of irradiation NR vulcanizates are almost linear (Figure 7), with the exception of a small initial region, in contrast to the relaxation curves of sulfur vulcanizates, which conform to an exponential law. This provides further confirmation that chemical relaxation in irradiation vulcanizates involves rupture of the molecular chains. Indeed, if it is assumed that the breakdown of chemical bonds in the chains is a first-order reaction, the relaxation rate should remain almost constant, as the breakdown of only a small proportion of the bonds in the molecular chains is sufficient for total destruction of the network. An approximate calculation performed by Priss[7] gives the following relationship between time and the number of chains per unit volume in the network:

$$N \approx 2\nu_0 [(1 - M_{av}/M) - kt/\nu_0] \tag{1}$$

From this an expression for stress relaxation is easily derived:

$$\frac{\sigma_t}{\sigma_0} = 1 - \frac{kt}{\nu_0 (1 - M_{av}/M)} \tag{2}$$

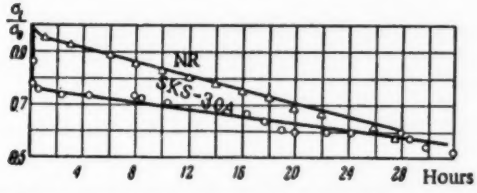


FIG. 7.—Stress relaxation of irradiation vulcanizates of NR and SKS-30A of the same network density (12×10^{19} ml^{-1}), obtained in air; Co^{60} source; NR, dose $75 \cdot 10^6$ r, maximum swelling 429%; SKS-30A, dose $90 \cdot 10^6$ r, maximum swelling 434%.

In Equations (1) and (2) ν_0 is the number of branch points per unit volume of the original vulcanizate; M_{av} is the average molecular weight of the chains in the original vulcanizate; k is the constant; σ_t and σ_0 are the values of the stress at time t and 0, respectively.

Equation (2) shows that if chain rupture takes place the relaxation curves should be linear and the constant rate of stress relaxation $k/\nu_0 (1 - M_{av}/M)$ should be inversely proportional to ν_0; this is in qualitative agreement with the relationship found for irradiation vulcanizates.

A more exact calculation[7] shows that at the last stage of the process (at $\sigma/\sigma_0 < 0.25$) the relaxation rate decreases and the linear relationship breaks down. The experimental data at our disposal are not sufficient to check this. The deviation from linearity at the start of the relaxation process should probably be attributed to relaxation processes associated with chain regrouping.

It also follows from Figure 6 that irradiation vulcanizates of purified natural rubber, obtained in air, have somewhat higher thermomechanical stability (lower relaxation rate constant) than vulcanizates with the same network density obtained in absence of oxygen. This may be attributed to addition of oxygen at some of the soluble bonds. This would decrease the number of diallyl bonds, with a consequent increase of the thermomechanical stability of the chains.

TABLE IV

DEGREE OF CRYSTALLINITY OF NATURAL RUBBER VULCANIZATES UNDER TENSION

Vulcanizates	Vulcanization time, min	Radiation dose in roentgens $\times 10^{-6}$	Max. swelling in xylene, %	Intensity ratio of crystalline interferences to amorphous scattering	Crystallinity at 400% extension
3.0% thiuram, without sulfur	10	—	525	1.2	44.5
3.0% thiuram, without sulfur	50	—	495	1.6	49
Diphenylguanidine 1.0% + sulfur 2.0%	10	—	720	1.0	41
Diphenylguanidine 1.0% + sulfur 2.0%	50	—	470	1.45	48
Irradiation vulcanization	—	30	759	1.1	42.5
Irradiation vulcanization	—	40	570	0.93	40

The tendency to crystallization under tension of irradiation vulcanizates of natural rubber was determined. The crystallinity of the stretched specimens was estimated by Field's method. It follows from the data in Table IV that irradiation vulcanizates made under the action of radiation with relatively small integral doses (up to $20–30 \cdot 10^6$ r) have the same degree of crystallinity as sulfur vulcanizates of the same network density. The crystallinity of the irradiation vulcanizates decreases with increasing radiation dose and the increase of cross-link concentration.

IRRADIATION VULCANIZATION OF FILLED RUBBER MIXTURES

It has been shown[3,4] that the usual vulcanizing agents, sulfur and accelerators, have no accelerating effect on irradiation vulcanization or even act as inhibitors (sulfur, thiuram). On the other hand, many investigators have noted that fillers have a strong effect both in irradiation and in chemical vul-

TABLE V

UNIFORMITY OF IRRADIATION VULCANIZATION OF A MIXTURE OF NR WITH 50 WT. PARTS OF CHANNEL BLACK, DOSE $32 \cdot 10^6$ R, Co^{60} SOURCE

Distance from upper surface, mm	0	5	10	15	20	25	30	35
Maximum swelling in xylene, %	455	463	468	489	484	426	441	431

canization. Therefore in the development of recipes for filled mixtures we used rubber-filler mixtures without chemical vulcanizing agent.

The filled mixtures, in the form of calendered sheets 0.2–0.3 mm thick interleaved with cellophane were placed in aluminum cases for irradiation vulcanization in the nuclear reactor, or in glass test tubes for vulcanization in the Co^{60} source. Technical vulcanizates were made by vulcanization in aluminum molds in the reactor, or in steel molds in the Co^{60} source.

Table V shows that irradiation vulcanization results in the formation of a uniform vulcanization network at all the thicknesses studied down to 40 mm, because of the high penetrating power of the radiation.

The introduction of carbon black gives irradiation vulcanizates with denser networks than in unfilled vulcanizates (Table I). The relative effects of different fillers on the density of the vulcanization network are the same as in ordinary chemical vulcanization. Active blacks of the channel type are the most effective. The introduction of fillers containing heavy atoms into mixtures of rubber with 50 parts of channel blacks not only failed to produce the increase of hardness which is to be expected from literature data[3,4], but even lowered the hardness somewhat and increased the maximum swelling (Figure 8). This effect is probably analogous to that observed in rubbers highly loaded with inactive fillers[8]. The hardness of irradiation vulcanizates increases steadily with the channel black content up to 100 wt. parts.

It was shown in our earlier investigations that both filled and unfilled sulfur vulcanizates made under the same vulcanization conditions have the same rate of chemical relaxation of stress. In contrast to this result, mixtures of rubber with carbon black have a considerably lower relaxation rate than unfilled mixtures, after irradiation vulcanization (Figure 9). The thermomechanical stability is higher in specimens with channel black than in specimens with the same amounts of furnace black. These results indicate that chemical bonds are formed between the rubber and the carbon black during irradiation vulcanization.

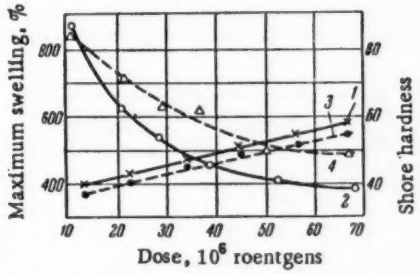


FIG. 8.—Effect of fillers on the properties of NR irradiation vulcanizates; Co^{60} source: *1*, *3*) Shore hardness; *2*, *4*) Maximum swelling in xylene; *1*, *2*) Rubber containing 50 wt. parts of channel black; *3*, *4*) Ditto, with 30 wt. parts of chalk.

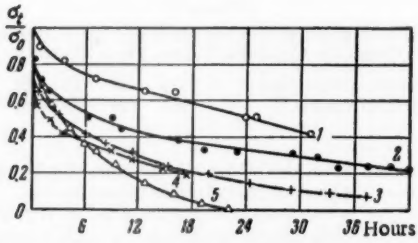


FIG. 9.—Relaxation of stress in rubbers and mixtures with carbon black (at 130°, $\epsilon = 60\%$, in nitrogen) after irradiation vulcanization in air in a nuclear reactor. *1*) NR without carbon black, $50 \cdot 10^6$ r; *2*) NR +40 wt. parts of channel black, 38.10^6 r; *3*) SKS-30A +40 wt. parts of channel black, $38 \cdot 10^6$ r; *4*) SKS-30AM +40 wt. parts of channel black, $38 \cdot 10^6$ r; *5*) SKS-30A without carbon black, $50 \cdot 10^6$ r.

The effect of resins of the styrene and epoxide type on the properties of mixtures based on NR and SKS-30AM mixtures containing channel black was studied. In contrast to sulfur vulcanizates, where the addition of resins results in an appreciable increase of hardness, in irradiation vulcanization these resins decreased the modulus and maximum swelling (Figure 10).

The irradiation temperature in irradiation vulcanization is significant. In a number of experiments increase of temperature increased the degree of cross-linking and the hardness of the vulcanizate.

Figure 11 shows variations of tensile strength, modulus, and relative elongation for irradiation vulcanizates of natural and of oil-filled butadiene–styrene (SKS-30AM) rubbers, containing 50 wt. parts of channel black, with the dose of energy absorbed. It is seen that the maximum tensile strength is found in vulcanizates made with the use of a dose of $40–50 \cdot 10^6$ r (in a Co^{60} source).

Table VI gives comparative data on the physicomechanical properties of irradiation vulcanizates made in the nuclear reactor, and of sulfur vulcanizates of the tire-rubber type, containing equal amounts of carbon black. The tire rubbers and the irradiation vulcanizates were tested under the same conditions, and the test specimens were all of the same size. The values for the irradiation vulcanizates are somewhat low, because molds were not used for vulcanization in this case.

Rubbers vulcanized by the action of nuclear radiations have low residual deformations, low dynamic loss and dynamic modulus, and high endurance in repeated extension. At the same time, irradiation vulcanizates have somewhat lower strength characteristics, especially those based on natural rubber. Irradiation vulcanizates have high resistance to oxidative degradation. Whereas

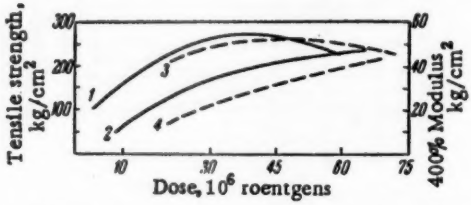


FIG. 10.—Effect of fillers on the properties of NR irradiation vulcanizates; Co^{60} source: *1*, *3*) Tensile strength in kg/cm²; *2*, *4*) 400% modulus in kg/cm²; *1*, *2*) Rubber with 50 wt. parts of channel black; *3*, *4*) Ditto, with 20 wt. parts of Polymer SS.

TABLE VI

PHYSICOMECHANICAL PROPERTIES OF RUBBERS

Mixtures	Irradiation vulcanization dose $38 \cdot 10^6$ roentgens						Tire rubbers				
	SKS-30A + 40 wt. parts carbon black		SKS-30AM + 40 wt. parts carbon black		NR + 40 wt. parts carbon black		SKS-30A + 40 wt. parts carbon black		SKS-30AM + 40 wt. parts furnace black	NR + 40 wt. parts carbon black	
	Channel	Furnace	Channel	Furnace	Channel	Furnace	Channel	Furnace		Channel	Furnace
Tensile strength in kg/cm²	130	112	115	78	150	157	294	236	261	274	321
Relative elongation, %	680	680	800	850	500	540	580	716	644	636	612
Residual elongation, %	16	12	16	20	8	8	24	21.6	33.6	33.2	32
Modulus at 200%, kg/cm²	15.6	23.6	8.3	21.4	35.6	28.5	49.0	32.0	34.7	26.8	53
Modulus at 400%, kg/cm²	62.6	69.0	39.0	53.5	136.5	132	152	85	102.5	104	100
Mechanical loss factor	15.3	15.8	9.5	9.5	7.3	7.0	35	18.5	24	17	10.6
Dynamic modulus	33.2	35.6	21.6	23.8	29	20.3	77	46.4	53	40.5	43
Endurance, in 1000 cycles in repeated extension E = 100% at 25°	127	336	285	1000	51.25	45.0	98	222	410	140	84

the tensile strength of the best sulfur vulcanizates of natural rubber falls to 15% of the initial value, and the relative elongation to 18%, after 12 hours at 130°, the corresponding values for irradiation vulcanizates are 58 and 81%, respectively. After 50 hours of aging at 130° the sulfur vulcanizates lose all their elastic properties, whereas the aging coefficients of irradiation vulcanizates under these conditions are 0.30 with respect to tensile strength and 0.70 with respect to relative elongation. The brittle point (−57°) of irradiation vulcanizates does not change during 12 hours of aging at 130°, whereas the brittle point of sulfur vulcanizates rises from −55 to −45°.

The data in Figure 12 also demonstrate the high stability of irradiation vulcanizates based on butadiene–styrene polymers. Under these conditions, sulfur vulcanizates show 50% decreases of tensile strength and relative elongation.

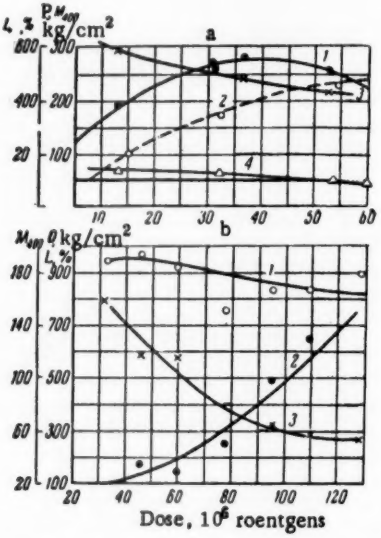


FIG. 11.—Effect of quantity of energy absorbed on the properties of irradiation vulcanizates containing 50 wt. parts of channel black: a) MR; b) SKS-30AM, Co^{60} source: *1*) Tensile strength in kg/cm²; *2*) Modulus at 400%, in kg/cm²; *3*) Relative elongation, %; *4*) Residual elongation, %.

SUMMARY

1. The structure and properties of irradiation vulcanizates of technical and purified SKB, NR, SKS-30A, SKS-30AM, and SKI rubbers with and without fillers, made by irradiation in a nuclear reactor and in a cobalt source, with integral doses of 10^7–10^8 r, have been studied.

2. The density of the network formed in irradiation vulcanization is determined by the quantity of energy absorbed, the type of rubber, the irradiation conditions (medium, temperature), and certain other factors.

The yield of crosslinks per 100 ev in air is ~12 for extracted butadiene–styrene rubber, ~4 for extracted NR, and 2.5 for technical SKS-30A. The

crosslinking effect increases with increase of temperature and decreases in presence of an oxidation inhibitor (phenyl-2-naphthylamine).

3. The thermomechanical stability of irradiation vulcanizates is superior to that of vulcanizates made with thiuram without sulfur, and such vulcanizates undergo the least changes in properties during chemical relaxation.

In contrast to sulfur vulcanizates, the relative rate of stress relaxation in irradiation vulcanizates depends on the density of the vulcanization network. This indicates the C—C type bridges are formed in the course of irradiation vulcanization. The thermomechanical stability of irradiation vulcanizates is raised by the introduction of active blacks.

4. The presence of carboxyl, hydroxyl, ether, and ester groups in irradiation vulcanizates of natural, butadiene–styrene, and sodium butadiene rubbers vulcanized in presence of air has been demonstrated by infrared spectroscopy. A dose of $60 \cdot 10^6$ r causes almost complete disappearance of double bonds from

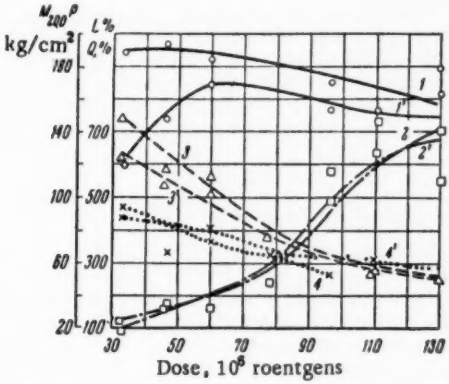


FIG. 12.—Variation of the properties of irradiation vulcanizates of SKS-30AM with 50 wt. parts of channel black during aging: *1*) Tensile strength; *2*) 200% modulus; *3*) Relative elongation; *4*) Maximum swelling; *1'*, *2'*, *3'*, *4'*) The same properties after aging.

extracted butadiene–styrene rubber. In the technical rubber, containing phenyl-2-naphthylamine inhibitor, this dose reduces the degree of unsaturation by about 30% of the initial value.

5. The tendency to crystallization on stretching was studied in irradiation vulcanizates of natural rubber. The crystallinity of irradiation vulcanizates made by irradiation with relatively small doses, up to $20–30 \cdot 10^6$ r, is the same as that of sulfur vulcanizates of the same network density. The degree of crystallization decreases with increasing radiation dose.

6. Conditions for the production of massive multilayer specimens by irradiation vulcanization were investigated. It was found that a uniform vulcanization network can be obtained irrespective of the thickness of the specimen (in the range 0.1–40 mm).

7. The physicomechanical and technical properties of irradiation vulcanizates were studied.

In comparison with the best sulfur with the same filler contents, irradiation

vulcanizates have a higher resistance to aging (4–5 times as high at 130°), low residual deformations, low hysteresis, high endurance to repeated deformation, and high heat resistance.

The tensile strength of irradiation vulcanizates, as a function of the radiation dose, passes through a maximum, but does not reach the values found in the best sulfur vulcanizates.

REFERENCES

[1] Charlesby, A., *Proc. Roy. Soc.* **A 222**, No. 1148, 60 (1954); Charlesby, A., RUBBER CHEM. & TECHNOL. **28**, 1 (1955); Charlesby, A., *Nucleonics* **14**, No. 9, 82 (1956).
[2] Jackson, W. and Hall, D., *Rubber Age* **77**, 865 (1955).
[3] Gehman, S. D. and Auerbach, I., *Inter. J. Rad. and Isotopes* **1**, No. 1, 2, 102 (1956).
[4] Kus'minskil, A. S., Nikitina, T. S. and Karpov, V. L., *Atomic Energy*, No. 9 (1956).
[5] Dogadkin, B. A. and Tarasova, Z. N., *Kolloid. Zhur.* **15**, No. 5, 347 (1953).
[6] Tobolsky, A., *J. Appl. Phys.* **27**, No. 7, 673 (1956).
[7] Prins, L. S., *Kolloid. Zhur.* **19**, No. 5, 607 (1957).
[8] Bryant, K. and Bisset, D., RUBBER CHEM. & TECHNOL. **30**, 610 (1957).

BULK POLYMERIZATION IN NATURAL RUBBER SWOLLEN BY METHYL METHACRYLATE *

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INTRODUCTION

Polymer-modified rubbers containing a substantial proportion of graft polymer have been prepared from natural rubber latex[1,2] using an amine-activated peroxide as initiator. Since dry rubber is cheaper than latex it is of interest to investigate the preparation of similar materials in a mass of dry rubber which has been allowed to imbibe the necessary quantity of monomer. The aims of this investigation were (*a*) to assess the conditions which obtain during such polymerizations, (*b*) to evolve a process which works within the limitations imposed by these conditions, and (*c*) to evaluate the products.

EXPERIMENTAL

CHARACTERISTICS OF POLYMERIZATION IN A MASS OF RUBBER

Peroxides as sole initiators.—Several instances have been reported of bulk polymerization in rubber swollen with vinyl monomers in which different initiators have been used and polymerization has been completed by heating for some time. This procedure was followed in some preliminary experiments in which rubber swollen with methyl methacrylate or styrene and containing a peroxide was heated at 80° or 100°. These experiments showed that conditions in the center of a reacting mass only 2 inches thick were nearly adiabatic, and that temperature control of the mass was virtually impossible, as is well known in other bulk polymerizations. Moreover, as the monomer was used up, increased crosslinking of the rubber by peroxide fragments occurred and at high conversions this was sufficient to render the product unworkable on the mill. In further experiments, therefore, the reaction was followed under nearly adiabatic conditions, and a catalyst system devised which would not lead to undue crosslinking of the rubber. These experiments were confined to methyl methacrylate because of its high heat capacity, low heat of polymerization, solubility in rubber, ability to polymerize in presence of rubber and suitable volatility.

Azobis-isobutyronitrile (AZBN) as sole initiator.—This initiator is not a crosslinking agent for rubber and was therefore not expected to cause loss of processability. Although in dilute solutions of rubber and methyl methacrylate in benzene no graft polymer is formed with AZBN as sole initiator[3], there was no information on concentrated solutions containing only rubber and methyl methacrylate.

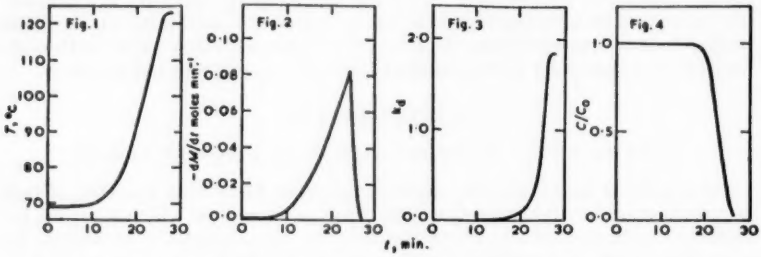
The experimental technique was to swell about 300 g of rubber with methyl methacrylate containing AZBN. The rubber could be cut sufficiently finely

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to give a homogenous mass without further mixing when the swelling was effected in a glass tube 2 inches in diameter, or the mass could be homogenized in a mixer (2 min mixing) and pressed by hand into a cylindrical shape about 2 inches in diameter. Under conditions of rapid polymerization this mass was large enough to give nearly adiabatic conditions in its center. The swollen rubber was heated in a Kilner jar in a bath at 70°, and the temperature rise in the ensuing reaction followed by embedding in the center of the mass a copper/Eureka thermocouple, whose leads were soldered to copper rods passing through bungs in a brass plate closing the top of the jar. The junction of the Eureka wire and copper rod provided a convenient constant-temperature junction.

If the reaction is adiabatic, the temperature rise is approximately proportional to the amount of polymer formed, and the rate of rise is proportional to the rate of polymerization. Further, the concentration and the rate of decomposition of catalyst at a time t from the start of the reaction can be calculated as follows:

The temperature dependence of k_d is known[4], k_d being the velocity constant for decomposition of AZBN. Hence k_d can be calculated for the temperatures



FIGS. 1–4.—Plots of reaction time, t, vs. (Figure 1) reaction temperature, T, (Figure 2) rate of polymerization, $-dM/dt$, (Figure 3) catalyst decomposition constant, k_d, (Figure 4) catalyst concentration, C/C_0. (Mixes contain: rubber 100, methyl methacrylate 55 and AZBN 0.25 part.)

reached at different times throughout the reaction. For the unimolecular decomposition of AZBN, where C = concentration of AZBN at time t

$$-\,\mathrm{d}\ln C = k_d dt$$

and

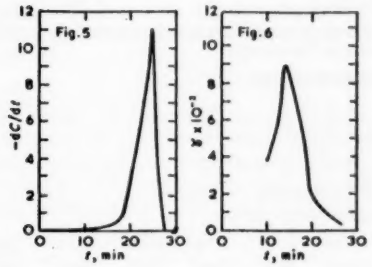
$$\ln C_0/C = \int_0^t k_d dt$$

Hence C can be found at any time of reaction by finding the area under the plot of k_d vs. t up to that time of reaction, and the rate of decomposition at that time then is given by

$$-dC/dt = k_d C$$

with the appropriate value for k_d.

If the rate of initiation is equated to the rate of catalyst decomposition, the kinetic chain length $\gamma = \dfrac{\text{rate of polymerization}}{\text{rate of initiation}}$, can be calculated at a particular time of reaction. Figure 1 gives a time/temperature curve for a typical



FIGS. 5 and 6.—Plots of reaction time, t, vs. (Figure 5) rate of catalyst decomposition, (Figure 6) kinetic chain length, γ.

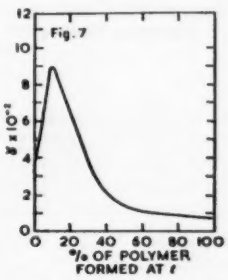


FIG. 7.—Kinetic chain length, γ, at time t, vs. % of total formed at time t (mixes as in Figures 1–4).

run using a mixture of 100 parts of rubber, 55 parts of methyl methacrylate and 0.25 part of AZBN. Figure 2 shows the rate of polymerization as obtained from Figure 1, knowing the total conversion of monomer to polymer. Figure 3 is a plot of k_d vs. t from which C/C_0 vs. t was obtained (Figure 4). Figure 5 shows the rate of catalyst decomposition, taken from Figure 4, and Figure 6 the kinetic chain length as calculated from Figures 2 and 5, plotted against time. Figure 7 shows γ plotted against per cent of total conversion. For mixes containing 100 parts of rubber, 115 parts of methyl methacrylate, and varying amounts of AZBN, Figure 8 shows the temperature plotted against time, and, superimposed, C/C_0 against time. Figure 9 shows γ plotted against degree of conversion for these mixes, and illustrates the rapid decrease in γ as the reaction proceeds owing to the rapid increase in rate of catalyst decomposition which accompanies a fall in monomer concentration. It should be noted that the calculation of γ takes no account of any effects on the rates of initiation or termination arising from the highly viscous nature of the reaction medium.

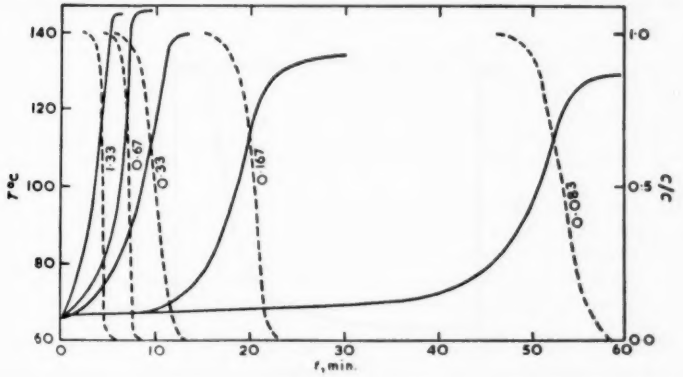


FIG. 8.—Reaction temperature T vs. reaction time t (full lines); catalyst concentration, C/C_0, vs. reaction time, t (broken lines) (mixes: rubber 100 parts, methyl methacrylate 115 parts, AZBN as shown on the figure).

TABLE I

PHYSICAL PROPERTIES OF VULCANIZATES OF RUBBER–POLYMETHYL METHACRYLATE PRODUCTS

Vulcanization recipe

	Parts
Rubber	100
Polymethyl methacrylate (PMM)	As in table
Zinc oxide	5
Stearic acid	1
Phenyl-2-naphthylamine	1
Cyclohexylbenzothiazolyl sulfenamide	0.7

(Vulcanized for 20 min at 140°)

Ratio rubber/PMM	52/47	71/29	70/30	51/49	51/49	52/48	53/47	54/46
Mode of preparation	Latex	Latex	Bulk	Bulk	Bulk	Bulk	Bulk	Bulk
Parts AZBN/100 rubber	—	—	0.25	1.33	0.67	0.33	0.167	0.083
T.S.[a], kg/cm²	177	230	213	115	133	136	116	111
E.B.[b], %	200	440	380	205	170	200	155	170
M.100[c], kg/cm²	135	48	37	73	106	101	96	91
M.300[d], kg/cm²	—	140	148	—	—	—	—	—
B.S.I. Hardness	98	87	73	99	92	85	85	74
Tear resistance at 120°, kg/mm	—	0.2	1.6	—	—	—	—	—

[a] = Tensile strength.
[b] = Elongation to break.
[c] = Modulus at 100% elongation.
[d] = Modulus at 300% elongation.

Figure 8 also shows that an upper limiting temperature of about 140° is imposed by the decomposition of all the AZBN, whatever its concentration.

Vulcanizate properties.—The physical properties after vulcanization of materials prepared in bulk with AZBN as sole initiator are shown in Table I in comparison with the corresponding materials (Heveaplus MG) prepared from latex with a peroxamine initiator[1,2]. While the "bulk" polymers are inferior in tensile properties, the tear resistance of a rubbery product (70 rubber/30 polymethyl methacrylate) is much better at high temperatures than that of materials from latex. In this respect the "bulk" polymers resemble the mixtures (Heveaplus MM) obtained by coprecipitation of preformed polymethyl methacrylate with rubber latex[2] rather than the graft polymers (Heveaplus MG) prepared by the peroxamine system from which the data in columns 1 and 2 of Table I were obtained. Characterization of the "bulk" polymers obtained

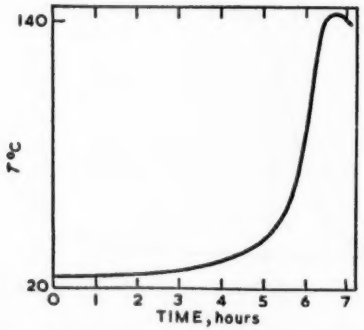


Fig. 9.—Kinetic chain length, γ, vs. % of total polymer formed at time t.
(Mixes as in Figure 8.)

by using AZBN as sole initiator shows in fact that they consist entirely of free rubber and free polymethyl methacrylate.

A MIXED CATALYST SYSTEM

The extent of polymerization required to raise an adiabatic system from one temperature to another can be easily calculated. From a product containing equal proportions of rubber and polymethyl methacrylate, an upper temperature limit of 140° coupled with high conversion requires the polymerization to be started at about 25°. This can be effected by using a mixed catalyst system comprising an activated peroxide to initiate polymerization up to about 50% conversion (i.e., until a temperature of about 80° has been reached) and AZBN to complete the polymerization. This obviates undue crosslinking of the rubber, most of which has been found to occur during the later stages of polymerization with peroxide initiators.

Initial experiments on the mixed catalyst system were carried out by taking half of the methyl methacrylate, dissolving in it the peroxide and AZBN and swelling half the rubber with the solution. The activator was added to the other half of the monomer, and this added to the other half of the rubber. After swelling overnight, the two halves were mixed in an internal mixer for 3 min, pressed into a roughly cylindrical shape, wrapped in cellophane and put

TABLE II

PHYSICAL PROPERTIES OF VULCANIZED RUBBER/POLYMER PRODUCTS MADE WITH MIXED CATALYST

Rubber polymer ratio.....	50/50	70/30	77/23
Tensile strength, kg/cm²	143	222	229
Elongations to break, %	135	425	480
M. 100, kg/cm²	129	46	31
M. 300, kg/cm²	—	150	112
B.S.I. hardness	96	78	70
Tear resistance at 120°, kg/mm	—	1.3	—

into a wide-mouthed vacuum vessel closed by a cork. The temperature was followed using a thermocouple inserted in the mass, and was registered on an Electroflo recorder. Alternative mixing techniques were to add the peroxide and AZBN to the already swollen mass in an internal mixer, followed by the activator, or to dissolve the peroxide and AZBN in all the monomer and add it to all the rubber, subsequently adding the activator in the mixer. On a large scale these different methods give different properties to the final material, arising from the different degrees of homogeneity obtained. The effect of inhomogeneity is to reduce the tensile strength and elongation of the vulcanizates.

By screening a number of peroxide/activator combinations on the basis of their ability to initiate and maintain polymerization in pure methyl methacrylate in lagged boiling tubes, two promising combinations were found; benzoyl peroxide/dimethylaniline, and *tert*-butyl hydroperoxide/tetraethylenepentamine/ferrous oleate. The latter was later rejected because it was not possible to avoid excessive crosslinking in a system containing rubber and because of its variable behavior. A typical mix using the former combination comprised 100 parts of rubber, 115 parts of monomer, 0.5 part of benzoyl peroxide and 0.5 part of dimethylaniline. The temperature rise was from 25° to 85° (i.e. ~ 50% conversion) and was no greater even when the amount of peroxide was doubled

or tripled. With the addition to the mix of 0.2 part of AZBN, an 87% conversion of monomer to polymer was obtained, giving an easily processable material containing equal proportions of rubber and polymer. Table II gives the properties of this material after vulcanization by the recipe of Table I, together with the properties of the vulcanizates obtained after dilution with smoked sheet to the levels of 70 rubber/30 polymer and 77 rubber/23 polymer. At the 70/30 level, good hot-tear resistance is shown, similar to that shown by the material of Table I, Column 3.

Figure 10 is a typical temperature record obtained with the mixed catalyst system, showing a long period when apparently no reaction is taking place, following which the temperature rises at first slowly and then rapidly to the upper limit of about 140°.

A serious problem in bulk polymerizations is the recovery of unconverted monomer from the polymeric system. It is therefore particularly convenient

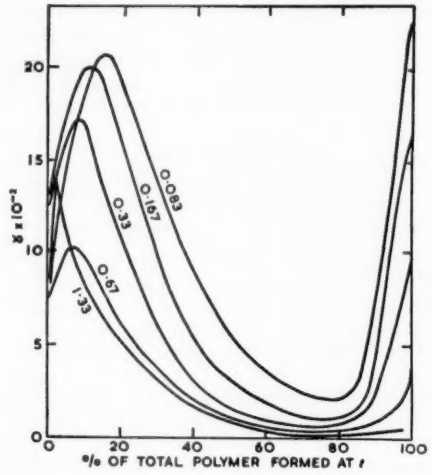


FIG. 10.—Reaction temperature, T, vs. reaction time, t. (Mix: rubber 100 parts, methyl methacrylate 115 parts and mixed catalyst system.)

that with the proportions of rubber and monomer used in the present experiments, most of the unconverted monomer volatilized out of the mass at near the maximum temperature and was thus directly recoverable by fitting a stillhead to the container. The proportions of 100 rubber/115 methyl methacrylate were about the optimum, the amount of residual monomer being increased by either increasing or decreasing this proportion of monomer.

Reproducibility of the process.—The effect of any variability in different samples of smoked sheet could be counteracted by adding a little calcium hydroxide. Too much of this has a deleterious effect on the properties of the vulcanizate, and to reduce the quantity to a minimum (0.05% on rubber) it was necessary to increase the amount of benzoyl peroxide by 50% and to dissolve it in the monomer before addition to the rubber so that it was in contact with the rubber throughout the whole of the swelling period. If the original proportion

TABLE III

EFFECT OF CALCIUM HYDROXIDE ON PROPERTIES OF VULCANIZATE OF RUBBER/POLYMER PRODUCTS

$Ca(OH)_2$/100 rubber	0	0.05	0.25	0.5	1.0	2.0
50 Rubber/50 polymethyl methacrylate						
Tensile strength, kg/cm²	145	151	146	112	109	102
Elongation to break, %	115	125	125	130	95	128
Modulus 100, kg/cm²	142	144	136	104	—	99
70 Rubber/30 polymethyl methacrylate						
Tensile strength, kg/cm²	233	223	230	218	232	127
Elongation to break, %	470	430	440	440	510	430
M.100, kg/cm²	46	48	48	49	40	27
M.300 kg/cm²	135	144	142	140	117	82

of the peroxide were added to the already swollen mass in a mixer, then the minimum effective quantity of calcium hydroxide was 0.5%.

Increasing the proportion of AZBN gave no increased conversion, and within wide limits had no effect on the properties of the vulcanizate. Variation of the proportions of benzoyl peroxide and dimethylaniline had little or no effect on the properties of the vulcanizate, either at the 50/50 level or after dilution with smoked sheet.

Vulcanizate properties.—Table III shows the effect of calcium hydroxide on the properties of the vulcanizate at the 50 rubber/50 polymethyl methacrylate and 70 rubber/30 polymethyl methacrylate levels (the latter mix was obtained by addition of rubber to the 50/50 material on the mill).

Table IV contains some other properties of vulcanizates prepared from material containing 70% rubber/30% polymethyl methacrylate which was obtained by adding rubber to a 50% rubber/50% polymethyl methacrylate material on the mill. 0.05% (on rubber) of calcium hydroxide was used in the preparation of the 50/50 batch.

Table V shows the effect of the Mooney viscosity of the original unswollen rubber on the modulus of the vulcanizate of a material diluted with smoked sheet to the 70/30 level.

Composition of the product.—Characterization of the material by the method of Allen and Merrett[5] has shown that about a quarter of the total polymethyl methacrylate is combined in a graft polymer (Table VI). This is as expected,

TABLE IV

PHYSICAL PROPERTIES OF VULCANIZATES OF 70 RUBBER/30 POLYMETHYL METHACRYLATE (0.05% CALCIUM HYDROXIDE ON RUBBER IN PRIMARY 50/50 PRODUCT)

Resilience (Dunlop Tripsometer)	57%
Compression set at constant strain	2 min rest 17.6%
	10 min rest 14.4%
	30 min rest 14.0%
Tension set (initial extension 50% of elongation to break)	2 min rest 20%
	10 min rest 16%
	30 min rest 15%
Flex cracking (De Mattia) to stage C	23.1 kc
Abrasion loss (Akron)	0.39 cc/1000 rev.
Tear resistance at 20°	3.1 kg/mm
100°	3.5 kg/mm
120°	2.1 kg/mm

TABLE V

MODULUS OF RUBBER/POLYMER PRODUCTS CONTAINING RUBBERS OF DIFFERENT MOONEY VISCOSITY

Mooney viscosity VR	87	68	56	40
M.300, kg/cm²	153	148	135	130

since roughly 50% of the polymethyl methacrylate is initiated by the peroxide, of which half should be free and half graft polymer.

LARGER SCALE BATCHES

Using the mixed catalyst system, a series of runs using 20 lb of rubber per batch showed a tendency for some inhomogeneity, accompanied by the formation of patches of almost pure polymethyl methacrylate on the surface of the batch or on the surface of internal voids. These hard lumps of polymer could not be dispersed during processing. To avoid their formation it was necessary to obtain good dispersion of the components of the catalyst system and to allow the monomer which boils off rapidly at the end of the reaction to get away readily from the surface of the mass. The first point was met by dissolving the peroxide and AZBN in 110 parts of methyl methacrylate before adding to 100 parts of rubber, and then adding the dimethylaniline in the remaining 5 parts of monomer. To allow the ready escape of monomer, the mass was wrapped in a heavily chalked calico cloth or a nylon cloth (preferably lightly chalked), and was then supported in a box or drum so that it did not touch the sides.

A 300-lb batch has been prepared as follows. Benzoyl peroxide (1.125 lb) and AZBN (0.15 lb) were dissolved in 165 lb of de-inhibited methyl methacrylate and 0.075 lb of calcium hydroxide was dispersed in this solution. The whole was added to 150 lb of rubber and allowed to swell overnight. Dimethylaniline (0.75 lb) in 8 lb of methyl methacrylate was then added to the swollen mass in an internal mixer. After mixing for 5 min the batch was divided in two, and each half pressed into a cylindrical block 17 inches in diameter and about 24 inches long. Each block was wrapped in lightly chalked nylon cloth and supported in a wire mesh cradle in a drum with a loosely fitting lid. Polymerization was complete in about 6 hours, with 88% conversion. The weight of monomer volatilized was 16 lb, leaving only 4½ lb of monomer in the mass. The tensile properties of the product when vulcanized according to the recipe of Table I are given in Table VII, together with the properties of the vulcanizates obtained after dilution with smoked sheet to the levels of 70 rubber/30 polymethyl methacrylate and 77 rubber/23 polymethyl methacrylate.

De-inhibition of monomer.—A simple method was evolved for removing inhibitor (0.01% hydroquinone) from large batches of methyl methacrylate. To a solution of 1 part of sodium hydroxide in 2 parts of water were added 8 parts

TABLE VI

CHARACTERIZATION OF THE "BULK" MATERIALS OBTAINED USING THE MIXED CATALYST SYSTEM

	Gel content, %	Free rubber, %	Graft fraction, %	Free polymer, %
Sample I	24	22	16	38
Sample II	13	24	23	40

of industrial alcohol followed by 5 parts of bentonite. After occasional stirring for at least 5 min the slurry was added rapidly with stirring to 1000 parts of methyl methacrylate and stirring continued for 5 min. The dark brown precipitate, containing 99.9% of the inhibitor, was then filtered off. The bentonite aids dispersion of the caustic soda solution and makes the efficiency of the de-inhibition largely independent of the efficiency of stirring. Other inert powders similarly aid dispersion, but do not give, like bentonite, a coherent easily filterable precipitate.

SUMMARY

Methyl methacrylate absorbed into dry natural rubber has been polymerized under conditions of low heat loss, using as initiator AZBN, alone or in combination with an activated peroxide.

With AZBN as sole initiator, some deductions are made from the change of temperature with time, as to the change in molecular weight of the polymer formed as the reaction proceeds. No graft polymer is formed.

TABLE VII

PHYSICAL PROPERTIES OF VULCANIZATES PREPARED FROM A LARGE BATCH OF 50/50 PRODUCT DILUTED WITH SMOKED SHEET

Rubber/polymer ratio	50/50	70/30	77/23
Tensile strength	136	220	232
Elongation to break	120	435	515
M.100	128	50	28
M.300	—	139	107
B.S.I. hardness	98	84	73

With the mixed catalyst system polymerization starts at room temperature. The process has been carried to a semitechnical scale, and some of the properties of the products are given. In general the materials resemble the corresponding materials prepared in natural rubber latex, but have markedly better hot-tear resistance. About 25% of the polymethyl methacrylate is present as a graft polymer.

SYNOPSIS

Methods are described for the preparation of polymer modified rubbers by bulk polymerization in natural rubber swollen by methyl methacrylate. The course of the reaction, using different catalyst systems, is followed by recording the temperature rise under conditions of low heat loss, and some suggestions are made as to the molecular weight of polymer formed at different stages of the reaction.

The polymer-modified rubbers are characterized by separation into their "free" and "graft" components, and their physical properties are described. A large-scale preparation is described where initiation of polymerization is sustained under conditions of low heat loss by the use of a mixed catalyst system.

ACKNOWLEDGMENTS

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REFERENCES

[1] Bloomfield, G. F., Merrett, F.M., Popham, F. J., and Swift, P. McL., *Proc. Third Rubber Technol. Conf.*, London, **1954**, p. 185.
[2] British Rubber Producers' Research Association, "Heveaplus M", Tech. Bull. No. 1 (1954).
[3] Merrett, F. M., *Trans. Faraday Soc.* **50**, 759 (1954).
[4] Bawn, C. E. H. and Mellish, S. F., *Trans. Faraday Soc.* **47**, 1216 (1951).
[5] Allen, P. W. and Merrett, F. M., *J. Polymer Sci.* **22**, 193 (1956).

THE SWELLING BEHAVIOR OF NATURAL RUBBER LATEX *

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INTRODUCTION

The distribution of a swelling agent among the particles of natural rubber latex is of interest in connection with several problems. A study by Morton, Kaizerman, and Altier[1] indicated that the equilibrium uptake of swelling agents by latex particles should increase with particle size, and experiments with polystyrene latex quantitatively confirmed their equation. From this it seemed likely that, in the case of a very heterodisperse latex such as natural rubber, the distribution of a swelling agent should be nonuniform, favoring the larger particles. This paper describes a test of this hypothesis, using as swelling agent a vinyl monomer methyl methacrylate. This choice was made because of interest in vinyl polymerization in rubber latex[2].

EXPERIMENTAL

The latex used was a 60% commercial concentrate, diluted to the concentration stated with 1.5% ammonia solution.

The monomer contents of latex particles of various sizes were obtained by making use of an oil-soluble dye Waxoline Blue (Imperial Chemical Industries Ltd.). If monomer containing 0.5%–1% of this dye is added to dilute (2% solids) latex, some of the monomer dissolves in the serum and a small amount of the dye is precipitated. This precipitate can be removed by filtration. It is assumed that the amount of monomer in an individual particle is proportional to the amount of dye in it, which can be estimated colorimetrically. The swollen latex is fractionated by a centrifuging technique and the monomer content of each fraction is measured from the color.

The detailed procedure is as follows. The latex was diluted to give a solids content of 2% and a suitable amount of monomer (containing 1% of the dye) was added. The latex was rotated end-over-end for several hours and then filtered. About 40 ml were placed in a centrifuge tube and centrifuged in a trunnion-type machine at 2000 rpm (measured with a stroboscope). The centrifuge was stopped at intervals and 2 ml of latex were removed from a fixed point in the centrifuge tube. The range of particle sizes corresponding to a given time of centrifuging was then calculated by Stokes' law; this is essentially the method of Nisonoff, Messer, and Howland[3]. It is convenient that the density of methyl methacrylate is close to that of natural rubber so that, for a fixed particle radius, centrifuging behavior is not much affected by monomer content. The successive fractions are cumulative, each containing all particles less than a given size.

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The 2 ml samples were dried and weighed in tared dishes. A small quantity of benzene was added to each dish, which was then covered and left until the dye was uniformly distributed; the amount of added benzene was checked by reweighing. The color of the benzene solutions was measured in a colorimeter (Hilger-Spekker). Calibration measurements with the dyed monomer at various concentrations in benzene enabled the amount of monomer in each dish to be measured. Control experiments in which a known amount of dyed monomer was added to latex, which was not subsequently fractionated, showed that the method for monomer estimation was quantitatively satisfactory.

RESULTS

It was first necessary to establish that natural rubber latex behaved qualitatively in the same way as polystyrene latex towards swelling agents. Figure 1 shows the swelling ratio Q measured as a function of time for (A) a whole

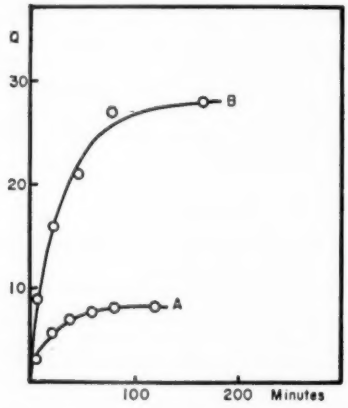


FIG. 1.—Uptake of swelling agent as a function of time. Comparison between whole latex (Curve A) and a large-particle fraction (Curve B).

latex; (B) a large-particle fraction from the same latex, obtained by fractional creaming with ammonium alginate[4]. The equilibrium uptake of methyl methacrylate by the large-particle fraction is substantially greater than that of the whole latex. The relative *rate* of swelling of the large-particle fraction is somewhat less, owing to the smaller surface area. The results of Figure 1 were obtained by rotating latex/monomer mixtures end-over-end at room temperature for varying times, followed by separation of the undissolved monomer by centrifuging.

Of more interest is the distribution of monomer among the latex particles in a whole latex, measured by the procedure described in the last section. Figure 2 shows the results for three different ratios of added monomer to latex, corresponding to swelling ratios of 1.3, 2.6, and 5.0. For larger amounts of monomer the swollen latexes were insufficiently stable for examination.

The particle radius scale is only semiquantitative, since its assessment depends on exact measurements of the geometry of the centrifuge, e.g., distance

from axis of rotation to sampling point, which are difficult to perform with the instrument used. The data represent 70% of the total latex; the smallest particles were not centrifuged under the conditions used. Two points should be borne in mind in examining Figure 2: (*a*) the *Q*-scale is cumulative, since each sample removed from the centrifuge contains all particles of sizes less than that plotted; (*b*) the particle radii are, of necessity, those for the swollen particles.

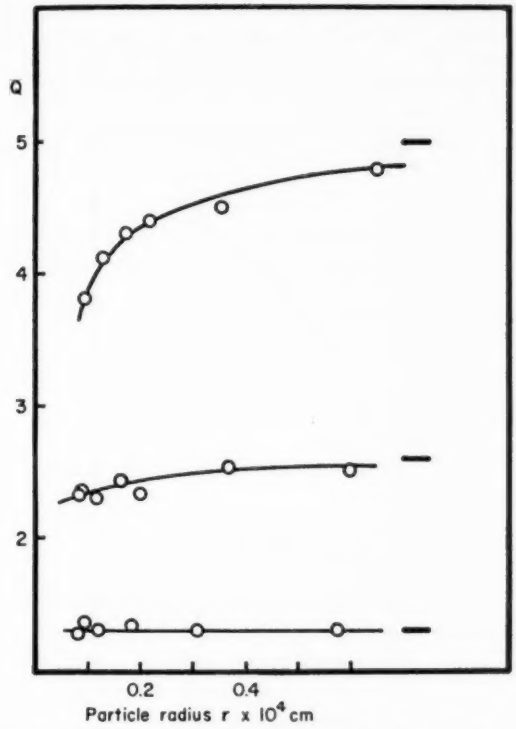


FIG. 2.—Cumulative values of Q as a function of particle radius. The heavy lines represent the overall values of Q for each experiment.

DISCUSSION

The thermodynamics of swelling of small particles has been evaluated by Morton et al[1]. The equation they derive is analogous to that for the swelling of a polymer network[5], the force opposing swelling being, instead of a network, the interfacial free energy between latex particles and serum

$$\Delta G = RT\,[\ln\,(1 - v_2) + v_2 + \chi v_2^2] + 2V_1\gamma/r = 0 \qquad [1]$$

where $v_2 = 1/Q$, is the volume fraction of rubber in the swollen particle; χ is the Flory-Huggins interaction constant; V_1 is the molar volume of the swelling

agent; γ is the interfacial energy; and r is the particle radius. Equation [1] predicts that the equilibrium swelling ratio will increase with particle size and will be very dependent on χ. Figure 1 shows qualitatively that the particles of natural rubber latex exhibit the expected behavior. Since the particle sizes in this case were not known, quantitative comparison is not possible.

The situation in the second experiment (Figure 2) is that where the amount of swelling agent absorbed is less than the maximum uptake possible. Under these conditions which were imposed by stability considerations, the free energy of swelling should be equal for every particle size, being given by nonzero values of ΔG from Equation [1]. In each experiment the value of ΔG at one particular experimental vaue of r (and v_2) was calculated from Equation [1]. This value

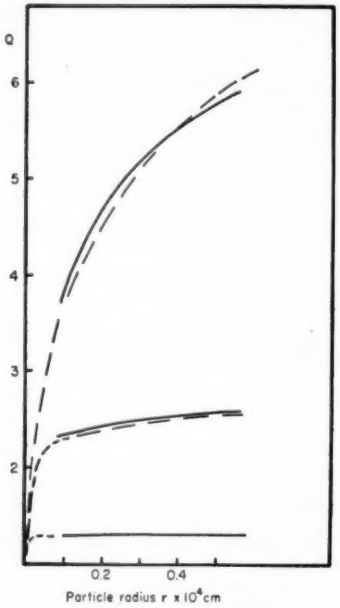


FIG. 3.—Theoretical values of Q as a function of particle radius. The solid lines are computed from the experimental values of $Q_{cum.}$.

of ΔG was then used, in conjunction with Equation [1], for the calculation of v_2 for othe rvalues of r. Figure 3 shows the resulting plot of Q against r for the three experiments of Figure 2. The broken lines in Figure 3 show the theoretical dependence. The experimental curves were obtained from the cumulative values of Q by using the relation

$$Q = Q_{cum.} + w \frac{dQ_{cum.}}{dw} \qquad [2]$$

where w is the total concentration (rubber + monomer) of each fraction.

For the theoretical curves, χ was taken as 0.5 and γ as 10 dynes/cm. These were considered to be reasonable values, though a closer fit could probably be obtained by adjustment. The agreement between the theoretical and experimental curves of Figure 3 provides additional evidence for the validity of the thermodynamic treatment of Morton and coworkers.

This work forms part of a program of research undertaken by the Board of The British Rubber Producers' Research Association.

ABSTRACT

The distribution of a swelling agent (methyl methacrylate) among the particles of natural rubber latex has been shown to be nonuniform. Large particles absorb more swelling agent than do small particles. The data are analyzed by means of the thermodynamic treatment of Morton, Kaizerman, and Altier.

REFERENCES

[1] Morton, M., Kaizerman, S., and Altier, M. W., *J. Colloid Sci.* **9**, 300 (1954); see the preceding and following articles, this issue.
[2] Bloomfield, G. F., and Swift, P. McL., *J. Appl. Chem.* **5**, 609 (1955).
[3] Nisonoff, A., Messer, W. E., and Howland, L. H., *Anal. Chem.* **26**, 856 (1954).
[4] Schmidt, E., and Kelsey, R. H., *Ind. Eng. Chem.* **43**, 406 (1951).
[5] Flory, P. J., "Principles of Polymer Chemistry", p. 576 ff. Cornell University Press, Ithaca, New York, 1953.

SWELLING OF LATEX PARTICLES *

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INTRODUCTION

It is generally agreed that the emulsion polymerization of water-insoluble monomers proceeds largely within the latex particles. These polymer particles are generally capable of imbibing monomer, which is continually being converted to polymer. Hence, in any kinetic studies, the composition of the growing particles is of prime importance. Although it is well known that the polymer particles in a latex will absorb an equilibrium quantity of monomer, it has not been established whether such an equilibrium is reached or maintained during the course of polymerization. Harkins[1] has pointed out that the attainment of such an equilibrium would depend on the relative rates of polymerization and diffusion of the monomer from the free monomer phase to the particles. However, no data are available on these relative rates in any of the systems studied. Furthermore, in the case where an equilibrium quantity of solvent is absorbed by a latex, the factors governing this equilibrium have not been well established.

Certain approximate values for the equilibrium monomer-polymer ratio have been determined for several different systems, both in this laboratory[2] and elsewhere[3,4], mostly in the course of kinetic studies. However, the variations which may be expected in the composition of these monomer-polymer particles and the parameters which control this composition have not been studied sufficiently. Smith[3] indicated what appeared to be a trend toward greater solubility of styrene in polystyrene latex of larger particle size. Harkins et al.[4] showed that the monomer-polymer ratio in a polystyrene latex decreased during the progress of a polymerization. A study of the factors governing this phenomenon has been made by Meehan[5]. In the course of his investigation, Meehan found that the equilibrium solubility of monomer in the polymer particles was a minor function of the molecular weight of the polymer or the amount of emulsifier on the surface of the particles, but appeared to be very dependent on the size of the particles. However, the available data are insufficient for definite conclusions on these points.

THEORETICAL CONSIDERATIONS

It is obvious that the phenomenon of equilibrium swelling of a latex particle in the presence of free solvent is analogous to the equilibrium swelling of a polymer network and can be treated in a similar fashion to the treatment of swelling[6,7]. If no networks are present in the polymer particle, the restraining force which counterbalances the swelling force is simply the interfacial free

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energy between the latex particle and the aqueous phase. Hence, when the swollen particle is in equilibrium with free solvent, the following conditions exist:

$$\Delta\bar{F}_1 = \Delta\bar{F}_{m_1} + \Delta\bar{F}_i = 0 \qquad [1]$$

where $\Delta\bar{F}_1$ = partial molar free energy of the solvent;
$\Delta\bar{F}_{m_1}$ = osmotic contribution to $\Delta\bar{F}_1$;
$\Delta\bar{F}_i$ = interfacial free energy contribution to $\Delta\bar{F}_1$.

The evaluation of $\Delta\bar{F}_{m_1}$ can be carried out by the familiar Flory-Huggins expression, viz.:

$$\Delta\bar{F}_{m_1} = RT\left[\ln(1 - v_2) + \left(1 - \frac{1}{n}\right)v_2 + \mu v_2^2\right]$$

where v_2 = volume fraction of the polymer in the swollen particle;
n = number average degree of polymerization;
μ = polymer-solvent interaction parameter.

The value of $\Delta\bar{F}_i$ can be deduced from a consideration of the increase in size of the interface as a function of the particle size and type of solvent. Thus, if r is the radius of the particle at swelling equilibrium, then let dr be the increase in radius caused by the imbibition of dn moles of solvent. The increase in surface area would then be $8\pi r dr$, and the increase in interfacial energy would be $8\pi r dr\gamma$, where γ is the value of the interfacial energy at swelling equilibrium. At the same time the increase in volume would be $4\pi r^2 dr$, which can also be written as dnM/ρ where M is the molecular weight of the solvent and ρ is its density. From this it follows that

$$8\pi r dr\gamma = \frac{2\,dnM\gamma}{\rho r} = \frac{2\,dnV_1\gamma}{r}$$

where V_1 = molar volume of solvent.

Hence the partial molar free energy contribution due to interfacial free energy can be expressed as

$$\Delta\bar{F}_i = \frac{2V_1\gamma}{r} \qquad [2]$$

At equilibrium, therefore, it follows from Equation [1] above that

$$\frac{2V_1\gamma}{rRT} = -\left[\ln(1 - v_2) + v_2 + \mu v_2^2\right] \qquad [3]$$

at high values of polymer molecular weight (n). Thus for a given polymer-solvent system, the swelling equilibrium of a latex particle should be a function only of its size, provided the interfacial energy is a constant quantity. Under such conditions, it should be possible to evaluate both μ and γ from a series of measurements, using the linear relation

$$-\frac{\ln(1 - v_2) + v_2}{v_2^2} = \mu + \gamma\frac{2V_1}{RTrv_2^2} \qquad [4]$$

With the above considerations in mind, a study was carried out of the equilibrium swelling of polystyrene latex particles by several solvents, as well as of the rate of swelling. In this study an attempt was made to maintain the interfacial tension (γ) at a constant value for any given solvent. Furthermore, to avoid complexities introduced by the distribution of particle sizes, the study was carried out on relatively homogeneous fractions of the latex obtained by fractional creaming.

EXPERIMENTAL PROCEDURES

MATERIALS

The materials used in preparing the polystryene latex and in the fractionation and solubility work were as follows:

Distilled water, boiled to remove dissolved oxygen and stored under nitrogen.
Nitrogen, Linde high purity.
Styrene, Dow Chemical Co., distilled at reduced pressure to remove inhibitor.
Potassium laurate, prepared from Matheson lauric acid and recrystallized twice.
Potassium persulfate, reagent grade.
Sulfole mercaptan, as supplied by Phillips Petroleum Co.
Potassium chloride, reagent grade.
Diisopropylbenzene monohydroperoxide, as supplied by Hercules Powder Co. and stated to contain 50% active peroxide.
Tetraethylenepentamine, as supplied by Carbide and Carbon Chemicals Corp., was distilled at 5 mm pressure and the fraction of b.p. 174–178° C was used.
Toluene, reagent grade.
Chlorocyclohexane, Eastman, b.p. 142–144° C.
Ammonium alginate, "Superloid" made by Kelco Co.

PREPARATION AND FRACTIONATION OF LATEX

Since substantial amounts of latex were required for this work, it was thought desirable to use the main fractions from latexes specially prepared to yield an average particle size close to the desired size. The recipes used and the results obtained are shown in Table I. The term D_s refers to the average

TABLE I
PREPARATION OF POLYSTYRENE LATEX

	Latex no.			
	103	102	106	104
Water	180	180	180	180
Styrene	30	100	100	100
Potassium laurate	5	5	5	1
Potassium persulfate	—	0.3	0.3	0.1
Sulfole mercaptan	—	—	0.3	
Potassium chloride	0.5	—	—	—
Diisopropylbenzene hydroperoxide	0.2	—	—	—
Tetraethylenepentamine	0.2	—	—	—
Temp. ° C	30	50	50	50
Avg. particle diam., D_s (A)	290 550 (D_w)	600	600	1600

particle diameter obtained by soap titration, and D_w refers to that obtained by light scattering, as described below. Latex 106 was made for the purpose of obtaining a latex of the same particle size as Latex 102, but having a much lower molecular weight in the polymer, owing to the presence of the chain-transfer agent (Sulfole).

The above latexes were subjected to fractional creaming by ammonium alginate, in order to obtain more homogeneous fractions. The fractionations were carried out in such a way as to remove the small particle size "tail" in the serum and the large particle size "head" in the cream. This made it possible to obtain a main fraction, representing between 20% and 50% of the original latex, and having a particle diameter close to the average diameter of the original latex. The amount of alginate required was determined for each latex and varied from 0.05% to 0.40% (based on latex weight). In each fractionation, the cream (bottom layer) was separated from the serum by centrifuging at 5000 rpm for 1 hour, after which the serum could be easily decanted. For the creaming process, each latex was adjusted to a dry polymer content of about 10%.

In the case of Latex 102, in addition to obtaining a main fraction (having a particle diameter of ca. 800 A), another smaller fraction was obtained (having a particle diameter of ca. 400 A). This was done in order to obtain data on the effect of particle size on polymer molecular weight in the *same latex*.

PARTICLE SIZE DETERMINATION

The particle size of the original latex was determined by the soap titration method of Maron et al.[8], whereas the particle size of the latex fractions was determined by means of light-scattering measurements with a Beckman Du spectrophotometer, using the method described by Maron and Ulevitch[9]. The soap titration method, which measures the volume-to-surface ratio of the latex particles, ordinarily yields an average diameter of a polydisperse latex which is referred to as a volume-to-surface average (D_s). It is defined as

$$D_s = \frac{\Sigma n_i D_i^3}{\Sigma n_i D_i^2}$$

The light-scattering method, on the other hand, yields a weight-average particle diameter (D_w) defined as

$$D_w = \left[\frac{\Sigma n_i D_i^6}{\Sigma n_i D_i^3} \right]^{\frac{1}{3}}$$

Since the latex fractions were assumed to be relatively uniform with regard to particle size, the average diameter should be the same by any method of measurement. As a means of testing the monodispersity of the latex fractions, an attempt was made to measure the particle diameters by the soap titration method as well. However, it was found that the alginate apparently interferes with this method by occupying part of the surface of the particles, thus leading to low results in the calculation of surface area. This was indicated by the fact that a determination of the initial soap present in the latex fraction, by conductimetric titration[10], showed consistently higher results (moles soap per gram polymer) than found for the original unfractionated latex. Since the fractionation involves several dilutions of the latex, it might be expected that

the soap content would be lower in the final fraction, owing to desorption from the surface of the particles. Hence it is strongly indicated that the alginate is interfering with the determination of soap content of the latex fraction, since ammonium alginate can react with the strong acids and bases used in this determination.

Under these conditions, it was impossible to determine the particle size of the latex fractions by soap titration. However, the fact that the creaming of the latex was quite sensitive to alginate concentration was an indication that relatively narrow fractions were obtained.

INTERFACIAL TENSION MEASUREMENTS

Surface tension and interfacial tension measurements were done with the duNouy Tensiometer. The surface tension measurements on latex were required for establishing the extent to which the surface of the particles was covered with soap molecules. In this way a latex was considered "saturated" with soap when the minimum surface tension value was attained.

Measurements of the interfacial tension between the latex (aqueous phase) and the swelling solvent were carried out in an attempt to evaluate the interfacial energy (γ) at the surface of the swollen latex particles. Since these swollen particles generally contain a high proportion of polymer (up to 50% by weight), it was also necessary to determine the interfacial tension between the latex and appropriate polymer solutions. However, with high molecular weight polystyrene, it is not possible to obtain fluid solutions containing more than about 10% polymer. In order to test the effect of higher concentrations of polymer on the interfacial tension of the solution, it was necessary to prepare polystyrene of lower molecular weight, by bulk polymerization with benzoyl peroxide. This polymer yielded a fluid solution in styrene or toluene at a concentration as high as 40%. Neither the high nor the low molecular weight polymer showed any appreciable effect on the measured interfacial tension between the latex and the solvent; hence the values of γ used were those obtained for the given solvent.

SOLUBILITY DETERMINATION

The equilibrium solubility of the solvents in the latex was measured as follows:

Twenty-five milliliters of the latex (diluted to a polymer content of about 10%), together with an excess of solvent, was placed in a 40-ml centrifuge tube. The tube was closed with a cork stopper and shaken for 1 hour, which was found to be ample for the attainment of equilibrium. Then a 4-in hypodermic needle was inserted through the cork so as to reach almost to the bottom of the tube. The latter was centrifuged at 2000 rpm for 30 minutes, resulting in a separation of the free solvent as the top layer. Then 10 ml of the solvent-saturated latex was withdrawn through the needle by a hypodermic syringe, and transferred to a 100-ml flask which was attached to a small distillation assembly. A few drops of acid were added to the latex (to prevent foaming), the latex frozen in a dry-ice mixture, the apparatus evacuated and sealed off. The solvent was then steam distilled over a steam bath, the solvent-water mixture being condensed in the receiver at ice-water temperature. The receiver was actually a long section of 7-mm glass tubing, so that the amount of solvent could be read volumetrically. The solvent-water interface was quite sharp and the height

of the solvent column could be read within 0.5 mm, representing 0.01 ml. Since the amount of solvent varied from 1 to 4 ml, this reading represented an accuracy of at least 1%. The distillation generally took about 4 hours, to ensure the collection of the last traces of solvent.

An important part of this work was the measurement of the swelling of latex particles whose surface was saturated with a monolayer of soap molecules. In order to do this, the above procedure was modified somewhat. First of all, the latex was titrated with soap, tensiometrically, to determine the amount of soap (potassium laurate) required to saturate the surface of the particles. Then the soap-saturated latex was saturated with the solvent as described above. However, as might be expected, the swollen particles should require additional soap to saturate the enlarged surface. Hence, an aliquot portion of the centrifuged latex was withdrawn through the needle and titrated with a soap solution to the minimum surface tension value. The correct amount of soap was then added to the whole sample of latex and the latter again shaken with excess solvent. This process was repeated until the surface tension values of the latex showed that no further addition of soap was required. This stepwise process was used in order to avoid having an excess of soap present at any time, since soap micelles might form and solubilize additional solvent. To minimize latex dilution, a 5% soap solution was used. Prior to use, the latex was neutralized to a pH of 10 to ensure that none of the soap was present as free fatty acid.

To determine the rate of solution of a solvent in the latex, 10 ml of the latex (containing 1 g polystyrene) was shaken in a graduated centrifuge tube with 3.5 ml of the solvent, at about 160 strokes per minute, for varying periods of time. After each shaking period, the tube was centrifuged for 5 minutes at 2000 rpm and the volume decrease of the solvent layer was noted. It was possible, at the beginning, to obtain a very sharp interface between the solvent and latex, so that the volume readings were accurate to within ± 0.02 ml. However, after about 1 hour of shaking, the interface became progressively more diffuse, decreasing the accuracy of the reading to ± 0.05 ml.

MOLECULAR WEIGHT DETERMINATION

The molecular weight of the polystyrene in each latex fraction was determined by measuring the intrinsic viscosity of the polymer in benzene at 30° C. The polymer was obtained by coagulating the latex in isopropanol. The viscosity measurements were carried out in a modified Ubbelohde viscometer, designed to permit several dilutions of the original benzene solution. In order to relate the intrinsic viscosity to the desired number-average molecular weight the following relation[11] was used:

$$\bar{M}_n = 178000\,[\eta]^{1.37}$$

This equation applies to polystyrene obtained at low conversions in bulk polymerization, but is sufficiently accurate for the molecular weight differences encountered in this work.

RESULTS

RATE OF SOLUTION OF TOLUENE IN POLYSTYRENE LATEX

The rate at which toluene is imbibed by a polystyrene latex is shown in Table II. This solvent was chosen for this work since it is close to styrene in

TABLE II

RATE OF SOLUTION OF TOLUENE IN POLYSTYRENE LATEX
(Latex fraction 102E, particle diam. 800 A, no added soap)

Time (min)	Toluene absorbed (ml/g polystyrene)	% Saturation of latex
5	1.00	61
10	1.25	76
15	1.40	85
20	1.55	94
90	1.65	100
210	1.65	100

molecular size and structure. Furthermore, if the diffusion rate seriously affects the solution rate, then this should be more apparent for a relatively large molecule like toluene, which is bigger than that of most monomers encountered.

It can be seen that the saturation of the latex with toluene is virtually complete after the first half-hour of agitation. This agrees with the findings of Meehan[5] that butadiene can saturate a polybutadiene latex within a period of 20 minutes. The result is not surprising in view of the enormous surface area presented by the polymer particles toward the diffusing solvent molecules. Hence it appears that the diffusion rate of monomers into latex particles should not affect the rate of polymerization, since the particles can be kept in a saturated condition, except in some very extreme cases. For instance, from Table II it can be seen that a polystyrene latex particle can imbibe its own weight of toluene in about 10 minutes. A rate of polymerization sufficiently rapid to outstrip this rate of solution would not generally be encountered. Thus it can be assumed, in most cases, that latex particles are maintained in a state of equilibrium solubility with regard to any free monomer phase present, and that the monomer-polymer ratio in the particles during polymerization is represented by this equilibrium solubility, as long as a free monomer phase exists.

EQUILIBRIUM SOLUBILITY IN POLYSTYRENE LATEX

To determine the factors which govern the phenomenon of equilibrium solubility in a latex, three solvents were used, i.e., toluene, styrene, and chlorocyclohexane. The last solvent was chosen for the particular reason that it is a much "poorer" solvent than the other two, and should be expected to have a higher μ value. Its rating as a poor solvent was based on a comparison of the precipitation temperatures of polystyrene in toluene and chlorocyclohexane. Using a polystyrene of about 4.5 million molecular weight in a concentration in

TABLE III

EQUILIBRIUM SOLUBILITY OF SOLVENTS IN POLYSTYRENE LATEX

	Latex fraction no.					
	103B	102E	102E[a]	102I	104C	106D
Particle diameter (A)	370	800	800	370	1730	840
Mol. wt. ($\bar{M}_n \times 10^{-6}$)	0.5	4.6	4.6	4.8	4.2	0.1
Solubility at 25° C (g/g polymer):						
Toluene	2.12	3.02	—	—	4.15	3.11
Styrene	1.81	2.93	1.50	—	4.60	—
Chlorocyclohexane	2.36	3.45	—	—	3.92	—

[a] Solubility measured with *no added soap*.

the vicinity of the theoretical critical volume fraction of polymer[12] (v_2 crit. $= \chi^{-1}$ where χ is the ratio of molar volumes of polymer to solvent), the precipitation temperature of the chlorocyclohexane was found to be about 260° K compared to 160° K for toluene, as determined by cooling experiments. Hence the chlorocyclohexane is a considerably poorer solvent than toluene.

The equilibrium solubility values found for the three solvents in latex fractions of different particle size are shown in Table III. The measured interfacial tension between the latex and the solvents was the same in all cases. The value obtained was 14 ± 1 dynes/cm when the latex was "saturated" with soap and 19 dynes/cm when no soap was added (Fraction 102E). The marked effect of added soap on the equilibrium swelling of the latex particles is shown very clearly in a comparison of the solubility of styrene in Latex Fraction 102E. Saturation of the particle surface with a layer of soap permits the particle to imbibe more than twice as much styrene as it would without added soap.

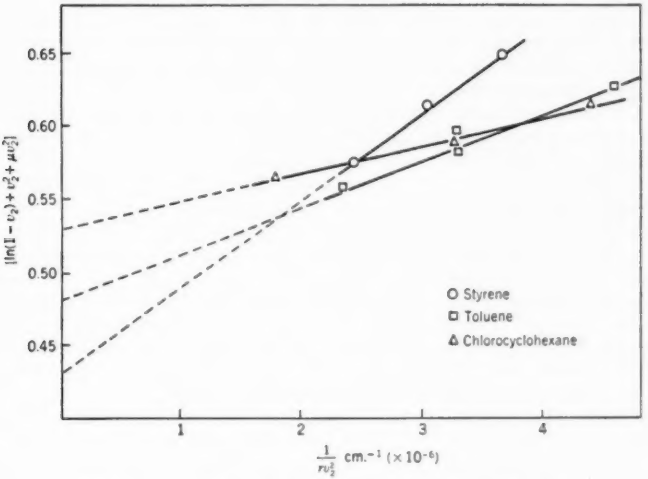


FIG. 1.—Equilibrium swelling of polystyrene latex particles at 25° C.

Fraction 106D was obtained from Latex 106, which was prepared specifically as a lower molecular weight polystyrene latex, in order to compare with Fraction 102E, which has a very similar particle size but a much higher molecular weight. The toluene solubility shows, as expected, that the polymer molecular weight is not a factor in the equilibrium solubility.

Fraction 102I represents a smaller particle size fraction obtained from the same original latex as Fraction 102E. It was used solely for a comparison of the molecular weight in large and small particles of the *same* latex. The data show no appreciable effect of particle size on molecular weight.

The equilibrium solubility data obtained for each solvent are shown plotted in Figure 1 in accordance with Equation [4]. This equation is, of course, based on the assumption that the interfacial free energy (γ) between the swollen particles and the aqueous phase is the same for all latex fractions and

any given solvent, provided the surface of the particles is "saturated" with respect to soap. For the calculation of the volume fraction of polymer in the swollen particles (v_2) the specific gravity of polystyrene was taken as 1.06 at 25° C and the volumes of polymer and solvent were considered as additive.

It can be seen from Figure 1 that, for all three solvents, the experimental points lie on a straight line, as predicted by theory. From the slope and intercept of each line the following values can be obtained for the parameters μ and γ:

Solvent	μ	γ (dynes/cm)
Styrene	0.43	4.5
Toluene	0.48	3.5
Chlorocyclohexane	0.53	2.1

The value of μ for toluene can be compared with the one quoted in the literature[13] of 0.44. From this, and from the high value obtained for chlorocyclohexane, it can be inferred that the above μ values are somewhat high. However, the fact that any reasonable values at all can be obtained for this parameter on the basis of the assumption made supports the validity of Equation [4]. The values for the interfacial free energy, γ, are all markedly lower than the measured value (ca. 14 dynes/cm) and indicate that the measured value obtained from a plane interface does not represent the true interfacial energy at the surface of these very fine particles.

It is interesting to note the decreasing order of solvent power from styrene to chlorocyclohexane, which might have been predicted on the basis of available knowledge. This seems to be accompanied by a decrease in the interfacial free energy, so that the poorest solvent has the lowest value for interfacial free energy. Since polystyrene is a hydrocarbon polymer, it might be expected that a poorer solvent would be more hydrophilic and hence show a lower interfacial free energy. This opposing effect of μ and γ would help to explain why the poorer solvent, chlorocyclohexane, exerts a greater swelling effect on the smallest particles than does styrene. Obviously the higher surface-to-volume ratio in these smaller particles is the deciding factor. Conversely, for the largest particles, the smaller surface-to-volume ratio decreases the effect of the surface energy, and styrene, therefore, shows the highest swelling volume. The intermediate-size particles (800 A) show a swelling volume which is not too different for all three solvents, apparently owing to a balance between the opposing effects of the μ and γ factors.

DISCUSSION

The experimental data show that, for any given solvent, the equllibrium solubility in latex particles is governed solely by the size of the particles and the interfacial energy between the particles and the aqueous medium. Thus the amount of solvent imbibed by the particles is a direct function of the particle size and an inverse function of the interfacial energy, in accordance with Equation [3] as predicted by theory.

The swelling of a latex particle by different solvents depends not only on the type of solvent (μ factor) but on the effect of the solvent on the interfacial free energy of the particles (γ). Thus in the case of a hydrocarbon polymer such as polystyrene, a better solvent apparently shows a higher interfacial energy; hence the expected increase in swelling is not obtained in the case of

the smaller particles, where the increased interfacial energy overrides the increased solvency effect. However, this relation between μ and γ may not hold for other polymers, especially those with polar functional groups.

It is interesting to consider the effect of Equation [3] on the monomer-polymer ratio in latex particles during the course of an emulsion polymerization, since it can be assumed that the particles are maintained in a saturated or near-saturated condition as long as any free monomer phase exists. For any given system, the expression on the right side of Equation [3] varies directly as the interfacial free energy (γ) of the particles and inversely as their radius (r). During the course of polymerization the particles increase in size, leading to an increase in γ, since the total amount of soap in the system is constant. If it is assumed that γ is thus directly proportional to the surface area of the particles, i.e., proportional to r^2, then the expression on the right side of Equation [3] is directly proportional to r. Hence, over a period of polymerization when the conversion is doubled, the radius of the particle only increases by a factor of about 1.25, i.e., an increase of about 25%. Since the function $-[\ln(1 - v_2) + v_2 + \mu v_2^2]$ increases about two or three times as rapidly as v_2 (when $\mu \sim 0.45$), then, in the above case, v_2 can be expected to increase about 10% for a 100% increase in particle weight. This helps to explain why, during any given polymerization, the monomer-polymer ratio in the particles changes very little, as long as a free monomer phase exists.

It is also interesting to note the effect of particle size on molecular weight of the polymer formed. According to the Smith-Ewart[14] treatment of the kinetics of emulsion polymerization, the molecular weight of the polymer is dependent solely upon the rate of entry of free radicals from the aqueous phase into the polymer-monomer particles. On the basis of diffusion the rate of entry of such free radicals would be directly proportional to the radius of the particle. Hence a smaller particle would capture fewer free radicals, leading to the formation of a higher molecular-weight polymer. However, in any given latex, the interfacial free energy should be approximately the same (per unit area) for large or small particles. Hence the monomer-polymer ratio will be a direct function of particle radius, being smaller for smaller particles. Thus the rate of polymerization in the smaller particles will be less than that in the larger ones (lower monomer concentration). This will offset the slower rate of entry of free radicals into the smaller particles, leading to similar molecular weights in both large and small particles, as found.

Finally, some conclusions can be drawn concerning the effect of particle size heterogeneity on the solubility of solvents in a latex. It is obvious from the method of derivation of Equation [3] that, for a polydisperse latex, the expression on the right side of Equation [3] is proportional not to $1/r$ but to $\Sigma n_i r_i^2 / \Sigma n_i r_i^3$, when n_i represents the number of particles having radius r_i. Hence v_2 is a function of the particle diameter as expressed by D_s, i.e., a volume-to-surface average diameter. Hence the particle diameter, D_s, as determined by soap titration, should give the best measure on which to base conclusions concerning the equilibrium solubility of solvents in the latex.

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ABSTRACT

A theoretical relation has been derived for the equilibrium swelling of latex particles. The equilibrium solubility and rate of solution of solvents were measured on a series of polystyrene latex fractions of varying particle size. The solvents used were styrene, toluene, and chlorocyclohexane.

It was found, as predicted by theory, that the equilibrium amount of solvent imbibed by latex particles is a direct function of the particle diameter and an inverse function of the interfacial energy at the surface of the particles. The molecular weight of the polymer has no effect on the equilibrium swelling, within the range from 100,000 to several million molecular weight units. The rate of imbibition of these solvents appears to be extremely rapid, indicating that equilibrium solubility would appear to be maintained in most polymerization reactions.

The fact that a particular solvent is a "good" solvent for the polymer does not necessarily result in a greater swelling of the particles, since the solvent may show a higher interfacial energy against the aqueous phase.

The soap titration method is best for determining the average particle size of a latex for purposes of predicting equilibrium swelling.

REFERENCES

[1] Harkins, W. D., *J. Am. Chem. Soc.* **69**, 1428 (1947).
[2] Morton, M., Salatiello, P. P., and Landfield, H., *J. Polymer Sci.* **8**, 215, 279 (1952).
[3] Smith, W. V., *J. Am. Chem. Soc.* **70**, 3695 (1948).
[4] Herzfeld, S., Roginsky, A., Corrin, M. L., and Harkins, W. D., *J. Polymer Sci.* **5**, 207 (1950).
[5] Meehan, E. J., *J. Am. Chem. Soc.* **71**, 628 (1949).
[6] Frenkel, J., *Acta Physicochim. U. R. S. S.* **9**, 235 (1938).
[7] Gee, G., *Trans. Faraday Soc.* **38**, 418 (1942).
[8] Maron, S. H., private communication.
[9] Maron, S. H., private communication.
[10] Maron, S. H., private communication.
[11] Mayo, F. R., Gregg, R. A., and Matheson, M. S., *J. Am. Chem. Soc.* **73**, 1691 (1951).
[12] Flory, P. J., *J. Am. Chem. Soc.* **73**, 1915 (1951).
[13] Huggins, M. L., *Ann. N. Y. Acad. Sci.* **44**, 431 (1943).
[14] Smith, W. V., and Ewart, R. H., *J. Chem. Phys.* **16**, 592 (1948).

SWELLING BEHAVIOR OF RUBBERS COMPOUNDED WITH REINFORCING PIGMENTS *

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INTRODUCTION

The effect of organic solvents on rubber in both its raw and vulcanized forms has been of practical interest to rubber technologists from the earliest days of the rubber industry. Since the solubility and swelling behavior of rubber undergo profound changes by vulcanization, these phenomena have also been of considerable interest in rubber research for estimating vulcanization rates and state or "degree" of cure. Over thirty years ago it was also recognized that the swelling maximum of rubber vulcanizates could be correlated with certain mechanical properties such as extensibility and hardness. In the special and more academic case of "pure" gum vulcanizates these relationships have in recent years been expressed in a quantitative, scientific manner by the statistical network theory of rubber elasticity and the thermodynamics of swelling. The "degree of vulcanization" or "state of cure" as generally conceived can now be expressed most effectively as the density of effective network crosslinks, a quantity easily calculated from equilibrium swelling or modulus determinations.

Although the effect of polymer network structure on swelling and modulus is clearly understood in the case of unfilled systems, the incorporation of fillers causes equilibrium swelling changes which have been the subject of considerable speculation. The fact that fillers reduce the equilibrium swelling volume significantly more than would be anticipated from the simple dilution effect on the polymer was recognized by Scott[1] as early as 1926.

It was also noted at this time that the reinforcing fillers, particularly carbon blacks, showed this property to a more pronounced degree than did the inert fillers. This phenomenon suggested a relationship between reinforcement and swelling since the reduction in swelling could be attributed to an increase in the amount of crosslinking or effective network chain density brought about by a chemical combination of polymer molecules with filler surface.

In 1949, Dannenberg[2] investigated the effect of a variety of carbon blacks (having a wide range of surface areas) on the reduction of equilibrium swelling volume of a synthetic rubber matrix. It was concluded that the particle size or extent of surface of these carbon blacks had little influence on swelling and, therefore, that possibility of rubber-filler chemical interaction at the interface was not indicated from these experiments. It was shown that the equilibrium swelling decrease of the matrix was greater with increased volume loading and that the "structure" blacks inhibited swelling more than other carbon black

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grades. Similar observations have recently been made by Kraus in a systematic study of the effective contribution of carbon blacks to network structure[13].

Another phenomenon involving the partial insolubilization of rubber in solvents by reinforcing fillers has been recognized for over thirty years. In recent years numerous investigators have studied this so-called "bound rubber" effect of carbon blacks because of the possibility that it was intimately associated with the mechanism of reinforcement. Dannenberg and Collyer[3] reported in 1949 that the quantity of bound rubber with a variety of carbon blacks was directly proportional to the external surface areas of the blacks determined from electron microscope examination. J. W. Watson[4] has recently confirmed these results. This suggests that some sort of interaction occurring at the carbon surface/rubber interface is responsible for the bound rubber effect.

The formation of bound rubber has been taken as proof by a number of investigators of chemical combination of rubber with carbon black. W. F. Watson[5] has attributed the formation of bound rubber to the attachment at the carbon surface of rubber free radicals produced during milling by mechanical chain breakdown. An explanation for bound rubber has been proposed by Endter[6] based on his observation of electron micrographs of the dried carbon-rubber gel which showed that the bound rubber was not attached to any significant degree to the carbon black surface. Endter suggests that the residual electric field surrounding each carbon black particle induces a polarization of the rubber double bonds resulting in crosslink formation in the immediate vicinity of the carbon black surface.

In regard to both the phenomenon of bound rubber formation in unvulcanized rubber and the reduction of equilibrium swelling of the rubber matrix in vulcanized rubber caused by small particle size reinforcing fillers, it has been unfortunate that most studies have been limited to very specific systems, usually carbon black and either natural or synthetic rubbers. It was felt that in order to have a rational basis for assuming that these phenomena were in some manner related to the mechanism of reinforcement, it would be of value to study a number of small particle size fillers in a variety of rubbers using different solvents. Data presented in this study show how general these effects are in a wide range of diverse systems. Another objective of this investigation was to compare the quantity of "effective crosslinking" produced by fillers in unvulcanized rubber from bound rubber gel swelling with the quantity of "effective crosslinking" in vulcanized rubber contributed by the same fillers from the reduction of rubber matrix swelling.

ORGANIC SOLVENTS AND FILLER MATERIALS

The solubility of a rubber in a solvent depends on the free energy level of the rubber in the solid state and in the solution. If the partial free energy is lower for the rubber in solution, then in the solid state it will dissolve. This means that rubber molecules will surround themselves by solvent molecules and move out into the solvent, whereas, at the same time, solvent molecules will penetrate into the rubber trying to separate the polymer chains. This process can only be completed when there are no strong bonds such as crosslinks between the polymer chains. High-energy bonds between the chains will restrict their mobility so that no chains can migrate into solution.

The penetration of solvent into the crosslinked network is initially unrestricted. However, after the polymer has imbibed a limited amount of solvent the swelling of the polymer is counteracted by the tension that builds up when

the chains are stretched between the crosslinks. The amount of solvent that will diffuse into the polymer until it reaches equilibrium is dependent on the number of crosslinks per cm^3 of polymer or expressed in a different way, on the average length of molecular chain between crosslinks. The larger is the number of crosslinks per cm^3, the shorter is the average length of chain betweeen crosslinks, and the lower is the amount of swelling. This degree of swelling can be expressed by the percentage increase in volume or by the volume fraction of the polymer in the swollen gel.

STUDIES OF SWELLING THERMODYNAMICS

The thermodynamics of swelling have been extensively treated by Flory[7], Huggins[8] and Gee[9]. Their studies allow calculation of the equilibrium swelling from the number of crosslinks per cm^3 and the μ factor. The latter is the interaction coefficient and depends mainly on the difference in cohesive energy density between the polymer and the solvent. The reduction in equilibrium swelling of rubber-filler systems due to the presence of filler was observed many years ago for natural rubber compounds. For these compunds aging and depolymerization play an important part and it is difficult to obtain clear-cut swelling equilibria[1]. Therefore, relatively little quantitative work was done on swelling of rubber-filler systems.

The work of Dannenberg on the effect of a variety of blacks on the equilibrium swelling in decalin showed small reductions in matrix swelling at increasing loadings of carbon black using various types of blacks. There seemed to be little difference among the blacks, which ranged from reinforcing channel black to nonreinforcing thermal blacks. Only the high structure type blacks, such as Acetylene and HAF, showed significantly lower matrix swelling figures.

The present study covers equilibrium swelling values in chloroform, benzene, heptane, and acetone. The compounds are made with natural rubber, SBR 1500, butyl rubber, neoprene, and nitrile rubber. The fillers used are channel and furnace blacks, fine silica of the precipitated and the fumed types, a synthetic silicate and a hard clay. The objective of this study is to determine whether the reduction of matrix swelling is a function of type of filler, type of rubber and type of solvent.

The effect of reinforcing fillers on swelling and bound rubber formation is particularly interesting in connection with the theory of reinforcement. The phenomenon of rubber reinforcement by fillers has been claimed to arise from some sort of strong linkages between filler particle and polymer. This means an additional hindrance to the mobility of the polymer chain which should manifest itself by a lower equilibrium swelling if these linkages are of a chemical nature. If the linkage is of a physical nature (adsorption, van der Waal's attraction, or hydrogen bonds), then we might expect the swelling values to be reduced in some weak solvents, whereas strong solvents should give swelling values practically unaffected by the presence of fillers. In the case of hydrogen bonds particularly it may be expected that polar solvents should disengage these bonds and therefore would not show matrix swelling data affected by the filler. Swelling in nonpolar solvents, on the other hand, should be strongly affected by loading with fillers or with those fillers that give rise to hydrogen bonds.

The calculations of Flory and Huggins allow us to determine the number of crosslinks per cm^3 and, in the case of reduction of equilibrium swelling, the additional crosslinks attributable to the filler effect can be calculated. This is an

extension of the theory which was not originally intended, and it is not to be taken as proof that actual chemical crosslinks are present. The application of the theory to filled systems does not serve the practical purpose of giving a quantitative expression for the effect of fillers on swelling.

BOUND RUBBER

The phenomenon of the insolubilization of part of the rubber by fine particle size fillers such as carbon black, even without any vulcanizing agent being present, has been observed by early investigators in the rubber technology field. With the growing use of synthetic rubber and oil furnace blacks the interest in the insolubilized rubber fraction increased[11]. The expressions "microgel," "carbon gel," and "bound rubber" were introduced and a relation between bound rubber and "reinforcement" was assumed[10]. Both phenomena apparently depended on the formation of linkages between carbon and polymer. The work of Stearns and Johnson[12] suggested that the surface of the black contained unsaturated groups which could be responsible for an actual chemical reaction during the mixing procedure or during vulcanization.

The present study of the butadiene-styrene copolymer SBR 1500 investigates the number of crosslinks per cm^3 of rubber matrix in the bound rubber gel fraction. The number of additional crosslinks that are found in the original compound after vulcanization and which are attributable to the presence of filler have also been calculated. These calculations have been made for white fillers and carbon blacks. It will be shown that the carbon blacks behaved in a way different from that of the white fillers investigated.

The main difficulty that exists in interpreting these data lies in the "state of cure" of the vulcanizates. The various fillers affect the rate of cure in degree, and possibly modify the nature and distribution of crosslinks. The swelling data are a measure for the degree of crosslinking (crosslink concentration) which is a quantitative expression for the state of cure.

In the attempt to separate these effects from the effect of filler-polymer interaction it is not possible to use exactly the same formulation for the different fillers and for different loadings in a single polymer. Most fillers, particularly the acidic ones, retard the vulcanization process at higher loadings and, if the same recipe and vulcanization time were used as for the lower loadings, the compounds would be definitely undercured. Longer periods of cure do not always give the same state of cure as does a faster curing compound at a shorter cure period because of the familiar phenomenon of reversion which results in a more branched chain network.

ADJUSTMENT OF ACCELERATORS

The method that has been followed here was to compare the swelling data of compounds that are cured to give maximum tensile strength at the temperature that is normal for the polymer and in a time that is about constant for all compounds of the particular rubber. This method is only possible if adjustments are made in acceleration. This has been achieved by adding a secondary accelerator such as the base, triethylene tetramine, to compounds with acidic retarding fillers (Cab-O-Sil). The amount of secondary accelerator depends on the nature and the loading of the particular filler and was determined experimentally in each case.

It is recognized that this method has its limitations, particularly in extreme cases. In practice, however, the adjustments in auxiliary accelerator do no

more than compensate for the retarding effect of such fillers as fumed silica, hard clay, and, to a lesser extent, precipitated silica and channel black. It has the advantage that a constant primary acceleration system can be used.

The formulations were chosen so as to give the same recipe for all fillers in one rubber with small adjustments in accelerator or activator to give the particular compound maximum tensile strength. Data are given in Table I.

TABLE I

FORMULATIONS OF COMPOUNDS TESTED FOR EQUILIBRIUM SWELLING VALUES

Natural Rubber

Basic Formula

	5 Vol.	10, 20, 30 Vol.
	Parts	
Smoked sheets	100.0	100.0
Stearic acid	3.0	3.0
Zinc oxide	5.0	5.0
Pine tar 600	3.0	3.0
Paraflux	—	2.5
Diethylene glycol	—	as indicated
Agerite Hipar	1.0	1.0
Sulfur	2.5	2.5
Santocure	as indicated	as indicated
Filler	as indicated	as indicated
Triethylene tetramine	as indicated	as indicated

		Pigment volume loading on Polymer			
		5%	10%	20%	30%
Fumed silica[1]	Parts	11.00	22.00	44.0	66.0
	Santocure	0.60	0.70	1.2	1.0
	Diethylene glycol	—	1.20	2.5	2.5
	Triethylene tetramine	—	0.25	0.5	0.8
Precipitated silica[2]	Parts	9.75	19.50	39.0	58.5
	Santocure	0.60	0.70	0.7	0.8
	Diethylene glycol	—	1.20	2.5	2.5
Calcium silicate[3]	Parts	10.50	21.00	42.0	63.0
	Santocure	0.60	0.50	0.5	0.6
	Diethylene glycol	.00	1.20	2.5	2.5
Hard clay[4]	Parts	13.00	26.00	52.0	78.0
	Santocure	0.60	0.70	0.7	0.7
	Diethylene glycol	—	1.20	2.5	2.5
	Triethylene tetramine	—	0.10	—	0.2
EPC Black[5]	Parts	9.00	18.50	37.0	55.0
	Santocure	0.60	0.50	0.6	0.7
	Diethylene glycol	—	1.20	2.5	2.5

TABLE I (*Continued*)

SBR 1500

Basic Formula

	Parts
SBR 1500	100.0
Stearic acid	2.0
XLC Magnesium oxide	1.0
Cumar MH 2½	10.0
Zinc Oxide XX78	5.0
Sulfur	2.5
Santocure	as indicated
Diethylene glycol	as indicated
Filler	as indicated
Triethylene tetramine	as indicated

		Pigment volume loading on polymer			
		5%	10%	20%	30%
Fumed silica	Parts	11.00	22.00	44.00	66.00
	Santocure	1.10	1.10	1.25	1.25
	Diethylene glycol	1.25	1.25	2.00	2.50
	Triethylene tetramine	0.45	0.90	1.70	2.50
Precipitated silica	Parts	9.75	19.50	39.00	58.50
	Santocure	1.10	1.10	1.25	1.25
	Diethylene glycol	1.25	1.25	2.00	2.50
	Triethylene tetramine	0.10	0.20	0.60	0.80
Calcium silicate	Parts	10.50	21.00	42.00	63.00
	Santocure	1.10	1.10	1.25	1.25
	Diethylene glycol	1.25	1.25	2.00	2.5
Hard clay	Parts	13.00	26.00	52.00	78.00
	Santocure	1.10	1.10	1.25	1.25
	Diethylene glycol	1.25	1.25	2.0	2.50
	Triethylene tetramine	0.23	0.45	1.3	2.00
EPC Black	Parts	9.00	18.00	36.00	55.50
	Santocure	1.10	1.10	1.25	1.25
	Diethylene glycol	1.25	1.25	2.0	2.50

Neoprene WRT

Basic Formula

	Parts
Neoprene WRT	100.00
XLC Magnesium oxide	2.00
Stearic acid	0.50
Neozone A	2.00
Zinc oxide	5.00
NA-22	except as indicated, 0.35
Cabflex Di-OA	as indicated
Filler	as indicated

TABLE I (*Continued*)

		Pigment volume loading		
		5%	10%	20%
Fumed silica	Parts	11.00	22.00	44.00
	Cabflex Di-OA	4.00	6.00	10.00
	NA-22	0.35	0.35	0.60
Precipitated silica	Parts	10.00	20.00	40.00
	Cabflex Di-OA	4.00	6.00	10.00
	NA-22	0.35	0.35	0.60
Calcium silicate	Parts	10.50	21.00	42.00
	Cabflex Di-OA	4.00	6.00	10.00
	NA-22	0.35	0.35	0.35
Hard clay	Parts	13.00	26.00	52.00
	Cabflex Di-OA	4.00	6.00	10.00
	NA-22	0.35	0.35	0.35
EPC Black	Parts	9.00	18.00	36.00
	Cabflex Di-OA	4.00	6.00	10.00
	NA-22	0.35	0.35	0.35

IIR 15

Basic Formula

	Parts
IIR 15	100
Zinc oxide	5
Stearic acid	2
ELA	1
Sulfur	2
Selenac	1
Methyl tuads	as indicated
Diethylene glycol	as indicated
Filler	as indicated

		Pigment volume loading on polymer			
		5%	10%	20%	30%
Fumed silica	Parts	11.0	22.0	44.0	66.0
	Methyl tuads	0.7	0.8	0.9	1.4
	Diethylene glycol	—	1.5	1.5	1.5
Precipitated silica	Parts	10.0	20.0	40.0	60.0
	Methyl tuads	0.5	0.5	0.6	0.7
	Diethylene glycol	—	1.5	1.5	1.5
Calcium silicate	Parts	10.5	21.0	42.0	63.0
	Methyl tuads	0.5	0.5	0.7	0.7
	Diethylene glycol	—	1.5	1.5	1.5
Hard clay	Parts	13.0	26.0	52.0	78.0
	Methyl tuads	0.7	0.8	0.9	1.0
	Diethylene glycol	—	1.5	1.5	1.5
EPC Black	Parts	9.0	18.5	37.0	55.5
	Methyl tuads	0.5	0.5	0.6	0.7
	Diethylene glycol	—	1.5	1.5	1.5

TABLE I (*Continued*)

Hycar 1042

Basic Formula

	Parts
Hycar 1042	100.0
Zinc oxide	5.0
Stearic acid	1.5
Spider sulfur	2.0
Dibutylphthalate	12.5
Picco 25	12.5
Altax	1.3
Methyl tuads	as indicated
Filler	as indicated
Triethylene tetramine	as indicated

		Pigment volume loading on polymer			
		5%	10%	20%	30%
Fumed silica	Parts	11.00	22.0	44.0	66.0
	Methyl tuads	0.15	0.3	0.3	0.3
	Triethylene tetramine	0.10	0.3	0.5	0.7
Precipitated silica	Parts	9.75	19.5	39.0	58.5
	Methyl tuads	0.10	0.3	0.3	0.3
Calcium silicate	Parts	10.50	21.0	42.0	63.0
	Methyl tuads	0.15	0.3	0.3	0.3
Hard clay	Parts	13.00	26.0	52.0	78.0
	Methyl tuads	0.15	0.3	0.3	0.3
	Triethylene tetramine	—	0.1	0.2	0.3
EPC Black	Parts	9.00	19.5	37.0	55.5
	Methyl tuads	0.15	0.3	0.3	0.3
	Triethylene tetramine	—	—	0.2	—

[1] Cab-O-Sil, Godfrey L. Cabot, Inc.
[2] Hi-Sil, Columbia-Southern Chemical Corp.
[3] Silene EF, Columbia-Southern Chemical Corp.
[4] Suprex Clay, J. M. Huber Corp.
[5] Spheron 9, Godfrey L. Cabot, Inc.

The mixing was done in a Banbury Type B at 140° F for smoked sheets and 120° F for synthetic rubbers. The batch size was about 1000 cm³. The milling cycle was as follows:

Minutes	
0	Put rubber into mixer
2	Add ZnO, MgO, ½ filler, ½ softener
4–6	Add remainder of filler and softener (Glycol and triethylene tetramine, if any)
8	Dump

The sulfur and accelerator were added on the roll mill at 140° F for natural rubber and 120° F for synthetic rubbers.

Data on the fillers used are given in Table II, and that on the matrix equilibrium swelling for the various compounds produced by the fillers in Table III.

TABLE II

PROPERTIES OF FILLERS USED IN EXPERIMENTAL FORMULATIONS

	Specific gravity	Average particle size, μ	Oil absorption, ml/g	Surface area, m^2/g	pH in 5% aqueous dispersion	Loss @ 105° C, %	Ignition loss 925° C, %	Nigrometer scale	Chemical composition	Moisture, %
Fumed silica	2.24	15–20	1.60	180	4.5	—	—	—	99% SiO_2	0.1–1.8
Precipitated silica	1.95	22	1.80	150	7.3	5	±9.0	—	87% SiO_2 0.5% CaO 0.2% Fe_2O_3 0.6% Al_2O_3 1.0% NaCl	—
Precipitated Ca silicate	2.10	30	1.30	80	10.0	5	15.0	—	64% SiO_2 18% CaO 0.15% Fe_2O_3 0.6% Al_2O_3 0.1% MgO 1.5% NaCl	—
Hard clay	2.60	500–2000	0.35	—	4.5–5.5	—	14.0	—	44–46% SiO_2 38.5% Al_2O_3	1 max.
EPC Black	1.85	30	1.00	100	3.8	0.5–1.5	5.2	85	94% C	—
HAF Black	1.85	35	1.30	65	9.0	0.5	1.6	90	98% C	—

TABLE III

MATRIX EQUILIBRIUM SWELLING OF EXPERIMENTAL COMPOUNDS IN VARIOUS MEDIA

Natural Rubber

		Chloroform	Benzene	Hexane	Acetone
Gum vulcanizate		460	370	265	18.0
Extrapolated matrix		—	—	—	—
Fumed silica	5%	760	420	310	15.1
	10%	535	400	290	14.7
	20%	535	440	330	14.0
	30%	485	415	305	16.8
Precipitated SiO_2	5%	695	380	285	14.8
	10%	505	380	270	13.5
	20%	620	500	390	17.5
	30%	685	500	410	22.0
Precipitated Ca metasilicate	5%	1110	590	460	13.0
	10%	600	450	325	14.5
	20%	610	470	355	18.0
	30%	560	415	305	17.0
Hard clay	5%	650	355	265	14.6
	10%	440	330	245	14.0
	20%	420	210	235	13.4
	30%	390	295	230	12.0
EPC Black	5%	625	355	270	14.1
	10%	550	410	300	13.4
	20%	470	370	275	13.8
	30%	390	295	220	14.0

SBR 1500

		Chloroform	Benzene	Hexane	Acetone
Gum vulcanizate		580	525	175	15.5
Extrapolated matrix		475	395	140	15.0
Fumed silica	5%	480	395	145	15.0
	10%	475	400	150	16.0
	20%	470	395	125	15.0
	30%	485	410	110	14.0
Precipitated SiO_2	5%	530	450	150	15.4
	10%	540	465	160	14.4
	20%	485	410	170	13.4
	30%	485	410	100	11.5
Precipitated Ca metasilicate	5%	520	430	145	16.0
	10%	505	425	150	14.9
	20%	475	480	180	14.0
	30%	455	390	100	13.3
Hard clay	5%	490	400	142	14.4
	10%	475	390	145	16.1
	20%	530	450	200	11.5
	30%	575	485	120	8.4
EPC Black	5%	635	470	155	17.3
	10%	535	445	155	17.9
	20%	425	350	160	14.9
	30%	365	320	90	13.6
HAF Black	5%	—	490	—	—
	10%	—	445	—	—
	20%	—	410	—	—
	30%	—	350	—	—

TABLE III (*Continued*)

Butyl Rubber

		Chloroform	Benzene	Hexane	Acetone
Gum vulcanizate		350	185	340	5.5
Fumed silica	5%	375	320	470	5.1
	10%	300	330	465	7.7
	20%	380	195	375	8.2
	30%	340	180	360	10.1
Precipitated SiO_2	5%	375	315	470	4.7
	10%	335	315	460	6.3
	20%	320	170	335	5.3
	30%	—	—	—	—
Precipitated Ca metasilicate	5%	400	320	485	4.9
	10%	335	280	455	6.2
	20%	315	170	320	5.4
	30%	285	160	300	6.8
Hard clay	5%	360	310	460	5.1
	10%	335	320	460	7.4
	20%	340	175	355	7.7
	30%	370	195	380	8.0
EPC Black	5%	345	305	450	5.3
	10%	310	310	440	7.0
	20%	295	160	305	7.8
	30%	290	165	300	6.5

Neoprene Rubber

		Chloroform	Benzene	Hexane	Acetone
Gum vulcanizate		520	450	56.0	48.0
Fumed silica	5%	555	465	55.0	41.0
	10%	585	485	57.0	45.0
	20%	460	380	—	32.0
	30%	305	295	52.0	36.0
Precipitated SiO_2	5%	490	415	58.1	39.7
	10%	530	445	55.1	42.6
	20%	465	360	48.4	33.5
	30%	—	—	—	—
Precipitated Ca metasilicate	5%	505	410	52.5	38.8
	10%	480	395	56.6	41.8
	20%	460	365	—	28.5
	30%	—	—	—	—
Hard clay	5%	580	475	50.0	39.0
	10%	625	520	56.0	43.0
	20%	500	415	—	32.0
	30%	—	—	—	—
EPC Black	5%	505	435	49.9	37.6
	10%	510	425	54.4	42.7
	20%	375	320	—	29.0
	30%	—	—	—	—

TABLE III (*Continued*)

Nitrile Rubber

		Chloroform	Benzene	Hexane	Acetone
Gum vulcanizate		630	290	25.1	250
Fumed silica	5%	660	320	18.0	275
	10%	660	275	6.3	250
	20%	635	270	4.3	260
	30%	650	270	5.4	270
Precipitated SiO_2	5%	515	320	15.5	275
	10%	730	300	3.9	263
	20%	738	277	2.2	266
	30%	750	305	4.6	281
Precipitated Ca metasilicate	5%	640	285	16.5	240
	10%	740	300	8.0	258
	20%	700	270	1.5	259
	30%	680	280	3.5	267
Hard clay	5%	655	305	16.8	275
	10%	740	304	8.1	265
	20%	770	290	6.4	270
	30%	720	295	6.2	265
EPC Black	5%	640	285	16.5	240
	10%	630	280	7.6	233
	20%	605	265	6.3	231
	30%	530	245	6.2	210

PROCEDURES

PROCEDURE FOR THE DETERMINATION OF PER CENT SWELLING BY VOLUME OF CURED RUBBER STOCKS

A weighed 1 × 2 inch specimen whose specific gravity is known is immersed in 100 ml of the solvent which is contained in a 250 ml test tube. The test tube and contents are then placed in a dark cabinet in a room in which the temperature is maintained at 70° F. The time lapse is seven days unless otherwise specified. At the end of the time interval, the specimen is removed from the solvent, lightly blotted dry, and quickly weighed in a preweighed bottle with ground glass cover.

Calculations:

$$\frac{\text{gain in weight}}{\text{gravity of solvent}} \times \frac{\text{gravity of specimen}}{\text{original weight of specimen}} \times 100 = \% \text{ swelling by volume}$$

Frequently used solvents and their specific gravities:

Benzene	0.879
Chloroform	1.498
Acetone	0.792
Hexane	0.660
Cyclohexane	0.779

PROCEDURE FOR DETERMINATION OF PER CENT BOUND RUBBER

Bound rubber is expressed as the amount (percentage) of the polymer in a compounded but uncured stock which fails to dissolve in benzene after standing for 24 hours.

Operational procedure.—The procedure of calculating bound rubber is as follows: A small strip is cut from the stock to be tested. Care is taken to trim all outer surfaces which may have been exposed to oxidation. The strip is then cut into 12 sections, total weight of which is 0.30 to 0.32 g.

Each section is now inserted on individual screen tiers. The screen is placed in the container and 100 ml of C. P. benzene are pipetted over the screen and into the container. The apparatus is kept in a place of constant temperature, 70° F, for a period of 24 hours.

At the end of this period, the benzene, containing any dissolved polymer, is withdrawn into a 250 ml flask. A 50 ml aliquot is transferred from the flask to a previously weighed 100 ml beaker. This solution is then evaporated to a point where all of the benzene but none of the polymer has been removed. The beaker is then desiccated and reweighed to determine the residue weight.

Calculation of per cent bound rubber is as follows:

$$\% \text{ Bound rubber} = 100 - \left(\frac{2A}{R} + 100\right)$$

where A = weight of dissolved polymer,
R = weight of polymer in original sample, and
$2A$ = total residue weight − that fraction of the residue weight attributed to benzene-soluble components of the compound.

Benzene swelling.—To determine benzene swelling with bound rubber, immediately after the benzene solution has been drained from the bound rubber apparatus, weigh 3 or 4 of the rubber gels (which have just been benzene extracted) into a preweighed weighing bottle which is quickly covered to prevent evaporation while weighing. After it is weighed, remove the cover and let it stand exposed to the air overnight. Cover again and reweigh.

Calculation of per cent benzene swelling is as follows:

$$\% \text{ Volume swelling} = \frac{(S.G. \text{ of gel})(\text{benzene weight})}{(S.G. \text{ of benzene})(\text{dried gel weight})} \times 100$$

$$\text{Specific gravity of gel} = \frac{\text{Weight \% of carbon black} + \text{Weight \% of bound rubber}}{\text{Volume \% of carbon black} + \text{Volume \% of bound rubber}}$$

Benzene weight = first weight − weight after evaporation

Swelling of the rubber matrix.—To calculate per cent volume swelling of the rubber matrix alone, the following equation is used:

$$\frac{\frac{S}{0.879}(L + Br)}{(T\text{-}S)\frac{Br}{S.G.}} \times 100 = \% \text{ swelling}$$

where S = weight of benzene absorbed by the gels (weight of saturated gels minus weight of gels after evaporation).
L = original carbon black (or reinforcing agent) loading (phr).
Br = per cent bound rubber,
$T\text{-}S$ = weight of dry gels (total saturated weight minus weight of benzene evaporated), and
$S.G.$ = specific gravity of polymer.

Sample calculation.—An example of the calculation of the per cent bound rubber follows: A residue of 0.799 g was obtained using original sample weight of 0.306 g. The following compounding recipe had been followed:

	Weight (g)	C_6H_6 soluble	C_6H_6 insoluble
SBR	500.5	—	500.5
Carbon black	250.0	—	250.0
Stearic acid	15.0	15.0	—
Pine tar	15.0	15.0	—
Sulfur	12.5	12.5	—
Santocure	2.5	2.5	—
Zinc oxide	25.0	—	25.0
Agerite Hipar	5.0	5.0	—
Total	825.5	50.0	775.5

Factors to be used in calculations:

$$\text{For solubles: } \frac{50}{825.5} = 0.0606$$

$$\text{For SBR: } \frac{500.5}{825.5} = 0.606$$

Calculations:

$$100 - \left[\frac{2(.0799\text{ g}) - .0185\text{ g}}{0.185\text{ g}} \times 100\right] = 100 - \left(\frac{.1413}{.185} \times 100\right)$$

$= 100 - 76.5 = 23.5\%$ bound rubber.

EFFECTS OF SOLVENTS ON SWELLING

The degree of swelling, in general, is highest with chloroform for all polymers except butyl rubber, for which the best solvent is hexane, followed closely by chloroform. The lowest swelling is found with acetone as a solvent, except in the strongly polar nitrile rubber, for which hexane gives the lowest swelling and acetone gives figures of the same order as benzene. The solvent power of benzene follows closely that of chloroform in all polymers tested here.

These differences reflect the drop in free energy of the solvent molecules when they move from their neighbors into the rubber. This is in turn determined by the changes in internal energy and entropy. The tendency of the solvent to swell the rubber is counteracted and finally stopped by the stretching of the chain network. Polar solvents, like acetone and chloroform, will have high swelling power for polar rubbers such as nitrile rubber and neoprene. Benzene, a nonpolar but very polarizable molecule, is a very good solvent for almost any polymer.

Compared with the effect of polymer-solvent interaction, the influence of fillers on swelling is relatively small and, since swelling data are difficult to reproduce, the filler effect sometimes does not amount to much above the average error of measurement. There are a number of effects, however, that can be detected without any doubt. These are:

(1) The matrix swelling of the rubber of highly filled compounds is usually smaller than that of the gum rubber. This means that the fillers have some restricting influence on the mobility of the polymer chains. Deviations from this rule are found at low and intermediate loadings and particularly in natural rubber where swelling is affected strongly by oxidation processes.

(2) There is a very pronounced decrease in matrix swelling with some fillers when the filler loading is increased. This is the case with carbon black, and, as Figure 1 shows, it is almost a linear function of the loading, particularly with the channel black. This effect is more pronounced with stronger swelling solvents; the very weak swelling agents show hardly any effect.

The nonblack fillers cause a reduction in matrix swelling which, however, does not seem to depend so much on the loading of the filler, as is the case with the blacks. There are some exceptions, however, with fumed silica (natural rubber—chloroform; neoprene—chloroform; neoprene—benzene) and hard clay (natural rubber—chloroform).

In a number of cases the effect of loading on the matrix swelling is negligible though the presence of the filler reduces the swelling of the vulcanizate at the lowest loading used here (5 per cent volume) as compared with the gum vulcanizate. In some cases small amounts of filler increase the volume swelling. The most pronounced cases of reduction in matrix swelling with loading are the following:

Natural rubber:	MPC black in chloroform and benzene; pyrogenetic silica in chloroform.
SBR 1500:	MPC in chloroform, benzene and hexane.
Neoprene WRT:	MPC in chloroform and benzene; pyrogenetic silica in chloroform and benzene.
Butyl rubber:	All fillers in benzene and, to some degree, in hexane; small effects in chloroform.
Nitrile rubber:	No large effects with any combination; a remarkable reduction is noticeable from 5 to 10 volumes of all fillers in hexane as a solvent.

This shows that the MPC black causes the effect in all rubbers and solvents except in Hycar, where all effects are small. In general, this effect will occur with all solvents in a polymer, though it may be less pronounced with the solvents that have small swelling values. These weak solvents would only break very weak linkages, whereas solvents with strong swelling tendencies would break stronger bonds.

If the effect of decreased swelling by increased filler loading were only noticeable with the weak solvents and not with the strong, it could be concluded that the fillers only contributed weak bonds. If, conversely, the effect were noticeable with strong solvents only, it would mean that the fillers only contributed strong

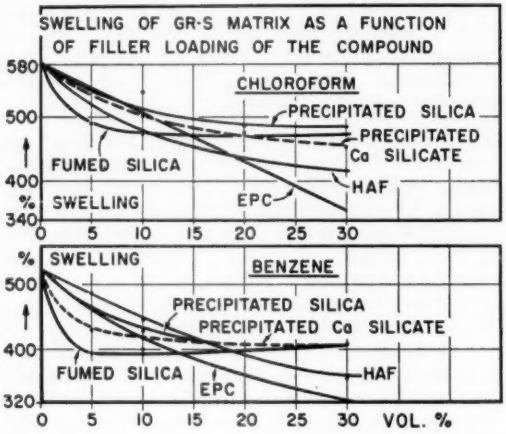


FIG. 1.—Swelling of styrene rubber matrix as a function of filler loading of the compound.

bonds. Actually the effect is noticed with both types of solvents, though it is more pronounced with the stronger solvents. In other words, the filler mainly causes formation of strong bonds, though apparently weaker bonds are also contributed.

BOUND RUBBER AND CROSSLINK DENSITY

Various authors have assumed that the phenomenon of bound rubber is related to reinforcement. Bound rubber, the rubber which is bound by the pigment to an insoluble gel after the pigment has been milled into the rubber, is determined by a standard procedure of extraction with benzene. During this extraction, the soluble rubber is separated from the insoluble rubber-black gel, which is highly swollen. It is logical to measure the degree of swelling of this fragile gel and determine the concentration of crosslinks of the rubber component of the swollen compound. The calculation does not presume anything about the nature of the crosslinks except that they are strong enough to withstand the forces exerted by the expansion due to the imbibition of the solvent.

Since we are mainly interested in the order of the effect as compared with swelling effects after vulcanization, the simplified Huggins equation was used without the refinement corrections:

$$\frac{\Delta F}{RT} = 0 = \ln v_1 + v_2 + \mu v_2^2 + \frac{\rho_2 V_1}{M_c} v_2^{\frac{1}{3}}$$

or

$$\frac{1}{M_c} = -\left(\frac{\ln v_1 + v_2 + \mu v_2^2}{\rho_2 V_1 v_2^{\frac{1}{3}}}\right)$$

$$\frac{\rho_2}{M_c} = -\left(\frac{\ln v_1 + v_2 + \mu v_2^2}{V_1 v_2^{\frac{1}{3}}}\right)$$

In this system the index 1 indicates the solvent and the index 2 indicates the

polymer. Here

$v_2 = 1\text{-}v_1$ = the volume fraction of the polymer, related to the degree of swelling Q (in per cent),

$$v_2 = \frac{100}{100 + Q},$$

V_1 = molecular volume of the solvent,

ρ_2 = density of the polymer,

μ = the interaction coefficient of the rubber-solvent system, and

M_c = average molecular weight of a chain length between two crosslinks.

It is realized that there may be objections to using the Huggins formula for such high degrees of swelling as occur in the bound rubber matrix, but here again, the desired degree of accuracy is not so high that this would interfere with the conclusions.

The entity $\frac{\rho_2}{M_c}$ is the moles of chains per cm³ and roughly $\frac{\rho_2}{2M_c}$ will be the moles of crosslinks per cm³. Again no correction is made for loose, floating chain ends.

Table IV compares swelling data of the vulcanizate matrix with those obtained on the bound rubber gel matrix for a number of SBR 1500 compounds. In both cases these data are also expressed in concentration of crosslinks,

TABLE IV

NUMBER OF CROSSLINKS IN VULCANIZED SBR 1500 COMPOUND MATRIX AND BOUND RUBBER MATRIX

	Vulcanizate			Bound rubber Matrix swelling		
Filler	Volume loading (%)	Matrix swelling (%)	$M_c \times 10^4$	(%)	(%)	$M_c \times 10^4$
EPC Black	0	525	44	—	—	—
	5	470	53	—	—	—
	10	445	58	6.1	10,800	0.09
	20	350	91	20.6	4150	1.15
	30	320	108	26.4	3300	1.7
HAF Black	5	490	48	—	—	—
	10	445	58	4.0	−(490)	(0.9)
	20	410	70	16.7	3300	1.7
	30	350	91	33.4	1780	5.0
Fumed silica	5	395	72	10.5	5700	0.7
	10	400	71	22.8	2700	2.5
	20	395	72	46.1	1230	9.6
	30	410	70	52.3	1030	14.0
Precipitated silica	5	450	57	—	—	—
	10	460	55	—	—	—
	20	410	70	17.3	3080	1.9
	30	410	70	25.6	2050	4.0
Precipitated Ca silicate	5	430	63	—	—	—
	10	425	64	—	—	—
	20	480	46	13.3	7000	0.45
	30	390	73	20.2	5100	0.79

computed by the Huggins formula above. This is done with two blacks and three white fillers, all at loadings of 5, 10, 20 and 30 per cent volume.

The first five compunds are made with EPC black and the swelling data indicate a steady increase of the concentration of crosslinks with increased loading. For the gum vulcanizate the molar concentration of crosslinks is 44 (per 10^6 cm^3); for the 30 per cent volume loaded vulcanizate it is 108 (per 10^6 cm^3) of the same units, an increase of 64 units.

Looking at the bound rubber values, it appears that even at 30 per cent volume loading the concentration of crosslinks in the gel matrix amounts to only 1.7 (per 10^6 cm^3). Since the percentage of bound rubber is only 26.4, the bound rubber crosslinks would only amount to

$$\frac{26.4 \times 1.7}{100} = 0.45$$

units. This indicates that the increase in crosslink concentration from 44 to 108, which occurs when the compound is loaded with 30 per cent volume of black, cannot be attributed to bound rubber crosslinks.

A similar picture is shown by the HAF black compounds. Here the 30 per cent volume black vulcanizate has 46 crosslinks (per 10^6 cc) more than the gum compound, whereas only

$$\frac{33.4 \times 5}{100} = 1.6$$

units may have been contributed by bound rubber under the conditions it was measured.

These two very obvious phenomena indicate that there must be an effect by carbon black on the vulcanization reaction which causes a higher concentration of crosslinks than is found in the absence of black and which is of a much larger order of magnitude than the crosslinkage found in bound rubber.

In the case of the white pigements, fumed silica, precipitated silica, and calcium metasilicate, the effect of loading on the crosslink density is less pronounced. For fumed silica, this value is practically independent of loading though higher than that for the gum vulcanizate. The bound rubber crosslinks form a significant percentage in the case of the 30 per cent volume loading vulcanizate. This, however, shows no higher crosslink density than the lower loaded compounds where bound rubber crosslinks are negligible.

Similar considerations hold for the two other white pigments; both show much lower bound rubber values and an approximately constant concentration of crosslinks in the vulcanizates at the different loadings.

The final conclusion from the above quantitative considerations is that the bound rubber phenomenon, as measured by the procedure outlined here, has no significant effect on the increased crosslinking of the rubber matrix of the vulcanized stocks resulting from the presence of fillers. The increased crosslinking occurs, therefore, during the vulcanization reaction.

SUMMARY

Equilibrium swelling data are presented for vulcanizates of natural rubber, SBR 1500, butyl rubber, neoprene, and nitrile rubber containing fumed silica, precipitated silica, precipitated calcium metasilicate, hard clay and carbon black. Swelling media are chloroform, benzene, hexane, and acetone.

It is observed that certain fillers, particularly carbon black, cause a reduction in the swelling of the rubber matrix which is commensurate with the volume loading of the filler. This effect is not specific for a particular solvent or elastomer.

When a series of loadings of a filler shows this effect of reducing the matrix swelling in one solvent, it is also shown by the swelling data for the other solvents, but not to the same degree.

The system SBR-benzene was studied to determine from the bound rubber measurements and the equilibrium swelling data for the corresponding vulcanizates the number of crosslinks per cubic centimeter in the unvulcanized and vulcanized states. It appears that the number of crosslinks estimated in the bound rubber gel is much too small to account for the increase in crosslink density in the rubber matrix that is caused by the presence of carbon black in the vulcanizate.

REFERENCES

[1] Scott, J. R., RABRM Lab Circular 26, London, **1924**; and 39, London, **1926**.
[2] Dannenberg, E. M., *Ind. Eng. Chem.* **40**, 2199 (1948).
[3] Dannenberg, E. M. and Collyer, H. J., *Ind. Eng. Chem.* **41**, 1607 (1949).
[4] Watson, J. W., *Trans. Inst. Rubber Ind.* **32**, 204 (1956).
[5] Watson, W. F., *Proc. Third Rubber Technol. Conf.*, London, **1954**, p. 553.
[6] Endter, F. W. and Westlinning, H., *Angew. Chem.* **69**, 219 (1957).
[7] Flory, P. J., *J. Chem. Phys.* **9**, 660 (1941); **10**, 51 (1942).
[8] Huggins, M. L., *J. Chem. Phys.* **9**, 440 (1941); *Ann. N. Y. Acad. Sci.* **43**, 1 (1942); *J. Phys. Chem.* **46**, 151 (1942); *Ind. Eng. Chem.* **35**, 216 (1943).
[9] Mark, H. and Whitby, G. S., Chapter II in "Advances in Colloid Science", Interscience Publishers, Inc., New York, **1946**.
[10] Baker, W. O., *Ind. Eng. Chem.* **41**, 511 (1949); Medalia, A. I., *J. Polymer Sci.* **6**, 423 (1951).
[11] Sweitzer, C. W. and others, *Rubber Age* **65**, 651 (1949).
[12] Stearns, R. S. and Johnson, B. L., *Ind. Eng. Chem.* **43**, 146 (1951).
[13] Kraus, G., *Rubber World* **135**, 67, 255 (1956).

COLORIMETRIC DETERMINATION OF AMINE ANTIOXIDANTS *

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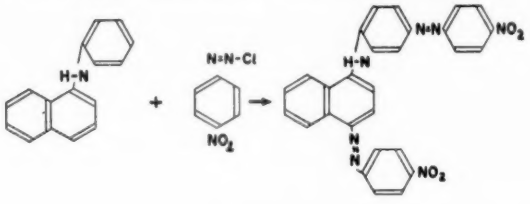
Separation of amine antioxidants from a mixture of compounding ingredients by steam distillation[5] or chromatographic techniques[1,7,8,9,12,16,17] has been reported. However, these techniques are tedious, require five or six man hours per separation, and use large quantities of solvents. Ultraviolet analysis of the proper fraction in the case of the elution technique will give the amount of amine antioxidant present. However, the ultraviolet absorption spectra of most amine antioxidants are so similar as to make identification by this means difficult. The identification of amine antioxidants is usually accomplished by color reactions[2,3,4,6,10,11,14,15]. The best of these color reactions appears to be the coupling with diazotized *p*-nitroaniline first reported by Burchfield and Judy[4]. This has been the basis for the qualitative and quantitative method developed in these laboratories[15].

A procedure using glacial acetic acid as the solvent and covering only ten of the common antioxidants has been developed by our personnel. Because of the severe blistering which can be caused by glacial acetic acid it seemed desirable to search for a more satisfactory solvent system. A study, described in this paper, was undertaken. At the same time, the coverage was extended to about thirty of the common commercial amine antioxidants. The solvent (acetone) reported by Mensik[13] for phenyl-2-naphthylamine was found to be unsatisfactory for most of the other antioxidants. The solvent system found to be most satisfactory was 25% concentrated hydrochloric acid and 75% methanol (by volume).

METHOD

The method of determining antioxidants described here consists of extraction of the antioxidant from the sample and formation of an azo dye by the use of a coupling agent. By the use of a spectrophotometer, the exact shade and intensity of color are measured—the former identifies the antioxidant and the latter determines its concentration.

The color formation is illustrated by the following example:



COLORLESS NEOZONE A | COUPLING REAGENT | AZO DYE

* This paper was presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Penna., March 5, 1958. Reprinted from *Rubber Age* **84**, 263–267 (1958).

The formation of dye differs from the usual commercial reaction in three ways. First, the dye is produced in minute quantities. Secondly, the reaction takes place in an organic solvent medium rather than in aqueous solution or suspension. Thirdly, a large excess of coupling agent has to be used, since the quantity and identity of the aromatic amine are unknown.

EXPERIMENTAL PROCEDURE

Apparatus.—All of the absorption measurements were made on a Cary Model II Spectrophotometer using quartz cells having a light path of 1.000 cm. The slit widths used were as shown in Table I.

Reagents.—The reagents used were:

Methanol—DuPont's pure synthetic methanol (99.85%).

Hydrochloric acid—Baker's "Analyzed Reagent" grade, specific gravity 1.188 (37.2% hydrochloric acid by weight).

p-Nitroaniline—Matheson, Coleman and Bell, m.p. 146 to 147° C.

Sodium nitrite—Baker's analyzed reagent grade.

Coupling agent—2.800 g (0.0203 mole) of *p*-nitroaniline is dissolved in 32 ml of hot concentrated hydrochloric acid and the solution is diluted with distilled water to 250 ml. After cooling to room temperature the volume of liquid is

TABLE I
SLIT WIDTHS USED IN THE DETERMINATION OF AMINE ANTOXIDANTS

Wavelength (millimicrons)	Slit width (millimeters)	Wavelength (millimicrons)	Slit width (millimeters)
350	0.054	550	0.006
375	0.029	575	0.006
400	0.017	600	0.008
425	0.012	625	0.012
450	0.009	650	0.018
475	0.007	675	0.027
500	0.006	700	0.043
525	0.006		

adjusted to exactly 250 ml. A second solution is made containing 1.44 g (0.0209 mole) of sodium nitrite in exactly 250 ml of distilled water. Both of the above solutions are reputed to be stable indefinitely. Twenty-five ml of each of these solutions are pipetted into separate 100 ml beakers and are chilled in ice to below 10° C. The contents are mixed by combining the solutions and pouring back and forth from one beaker to the other. Pure nitrogen is bubbled through the mixture as it is allowed to warm to room temperature. Finally, ten mg of urea (or one ml of 0.1 g/10 ml solution) is added to destroy any excess nitrous acid. The reagent becomes cloudy after an hour or so but is suitable for use for several hours. Fresh reagent should be made every day.

Preparation of methanol-hydrochloric acid solvent.—Three volumes of methanol are placed in a glass stoppered bottle and one volume of concentrated hydrochloric acid is added gradually with gentle mixing. The mixture is allowed to come to room temperature before carrying out the analyses.

Procedure.—The sample to be analyzed must be very thinly sheeted (or powdered by passing through a Wiley Mill). Weigh a 1.0000 ± .0005 gram sample. Wrap with extraction cloth which has been previously extracted to remove sizing, etc. Place in an Underwriter's extraction cup and extract for 16 hours with 95% ethanol or methanol. Transfer the alcohol extract to a

SPECTRA OF DIFFERENT ANTIOXIDANTS

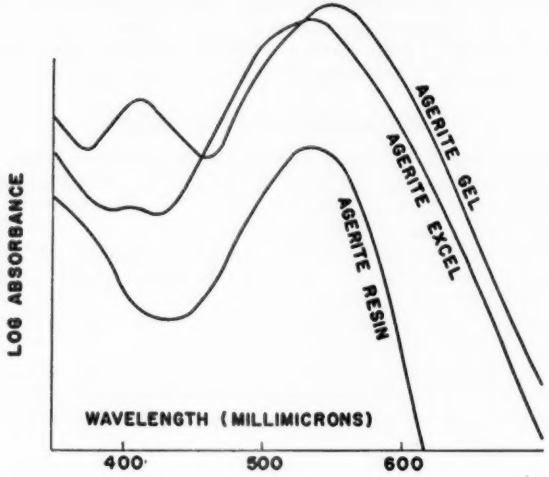


FIG. 1.

100 ml volumetric flask. Cool to room temperature and bring to the mark with the extraction solvent. Transfer a ten ml aliquot to a 100 ml volumetric flask. Add 15 ml methanol-hydrochloric acid solution and one ml of coupling agent. Place in dark for 1½ hours and then bring to the mark with methanol-hydrochloric acid. Determine the absorption spectrum from 700 millimicrons

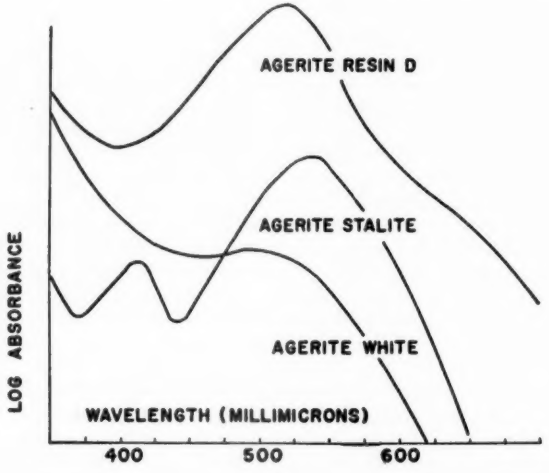


FIG. 2.

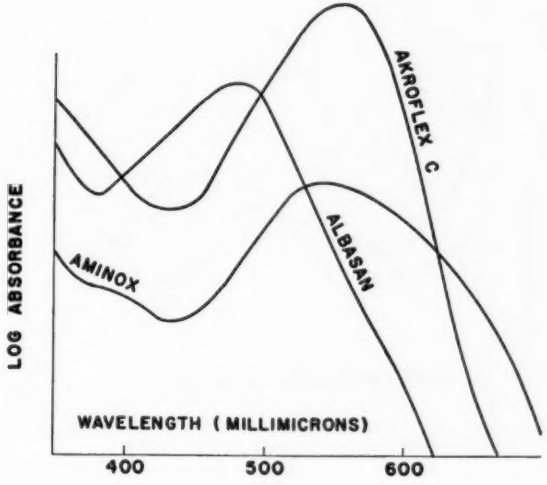


FIG. 3.

to 350 millimicrons using a Cary Spectrophotometer. (Note: Other spectrophotometers may be used with proper calibration.)

Plot the absorbance readings on Keuffel and Esser semilogarithmic graph paper 359-H-71, 3 cycles × 10 to the inch. Compare the resulting spectrum with Figures 1 through 9 for identification of the antioxidant. (Note: If a red color is formed immediately upon coupling and the color then fades to an amber

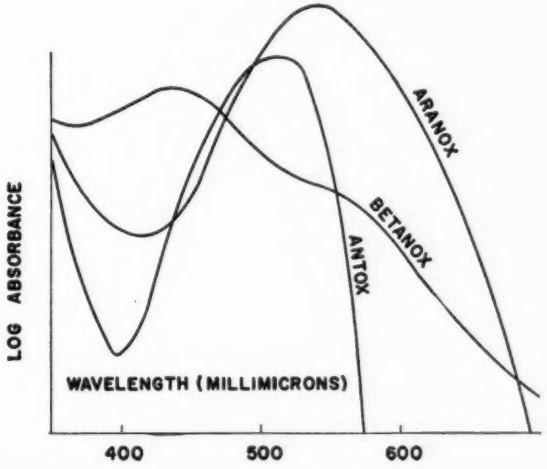


FIG. 4.

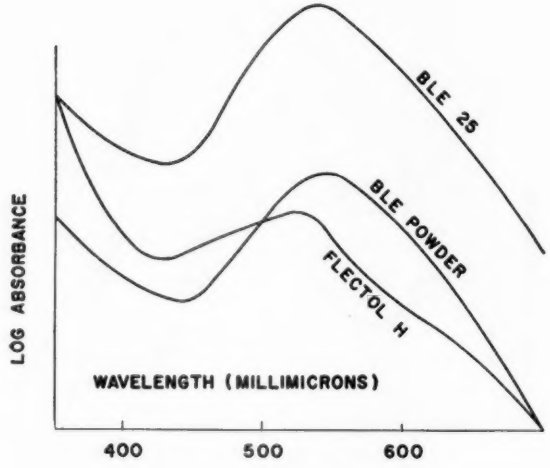


FIG. 5.

or brown, it is likely that one of the antioxidants containing phenyl-2-naphthylamine (PBNA) is present. In this case an alternate procedure must be used.)

Alternate procedure for PBNA.—Extract as indicated in the regular procedure. Take a ten ml aliquot from the 100 ml volumetric flask. Bring almost to the mark with methanol-hydrochloric acid mixture and add one ml of

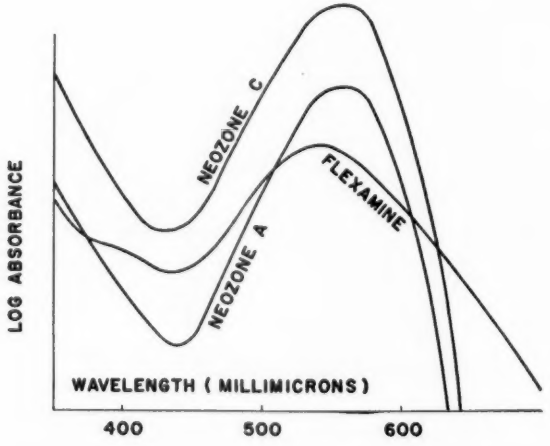


FIG. 6.

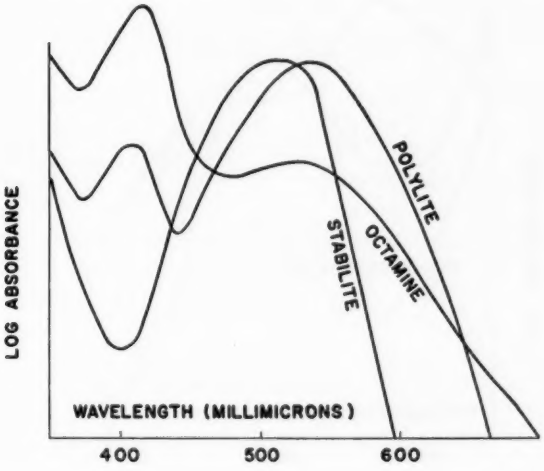


FIG. 7.

coupling agent. Bring exactly to the mark, mix and immediately determine the absorbance. The absorbance will rise to a maximum in 2 to 5 minutes after coupling. Use this maximum absorbance in calculating the amount of antioxidant present. Calculate per cent antioxidant using the equations in Table III.

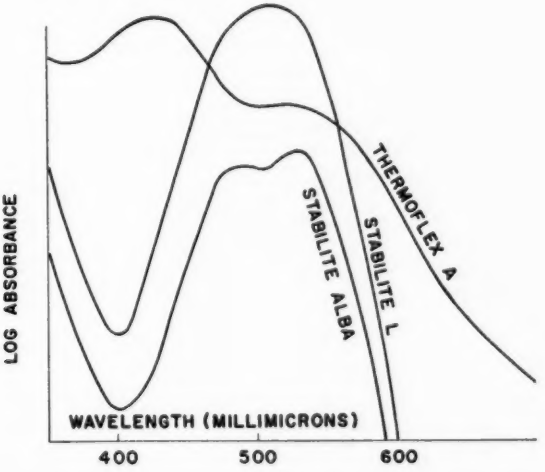


FIG. 8.

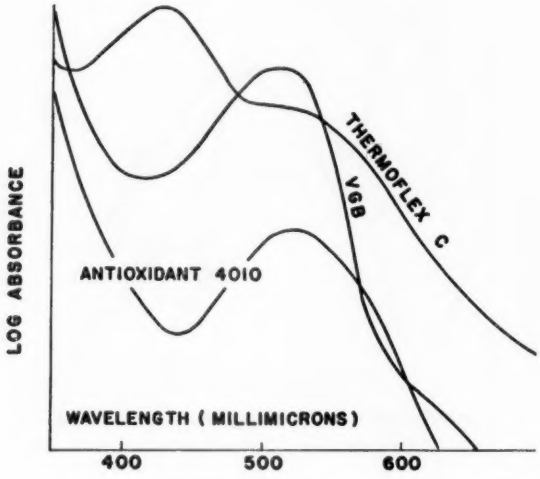


FIG. 9.

Development of equations.—The equations are developed as follows:

$$\text{Let } W = AC \tag{1}$$

where W = weight of antioxidant in grams,
A = absorbance at the wave length concerned, and
C = concentration in grams of antioxidant per 100 ml required for absorbance of 1.000.

Then

$$\% \text{ Antioxidant} = \frac{100\ (AC)}{0.1\ (\text{sample weight})} \tag{2}$$

TABLE II

EQUATIONS FOR ANTIOXIDANTS WHICH CAN BE DETERMINED BY THE REGULAR PROCEDURE

Antioxidant	Equation % antioxidant =	Antioxidant	Equation % antioxidant =
Agerite Excel	$1.30\ A_{534}$	Flectol H	$3.02\ A_{525}$
Agerite Gel	$1.76\ A_{535}$	Flexamine	$1.61\ A_{540}$
Agerite Resin	$1.13\ A_{534}$	Neozone A	$0.443\ A_{557}$
Agerite Resin D	$3.10\ A_{522}$	Neozone C	$0.606\ A_{557}$
Agerite Stalite	$1.37\ A_{537}$	Octamine	$3.79\ A_{419}$
Akroflex C	$0.778\ A_{555}$	Polylite	$2.07\ A_{537}$
Albasan	$3.99\ A_{495}$	Stabilite	$1.40\ A_{522}$
Aminox	$1.18\ A_{547}$	Stabilite ALBA	$0.668\ A_{522}$
Antox	$1.49\ A_{512}$	Stabilite L	$0.573\ A_{515}$
Aranox	$0.902\ A_{540}$	Thermoflex A	$2.98\ A_{425}$
*Betanox	$3.13\ A_{438}$	Thermoflex C	$2.87\ A_{425}$
BLE-25	$0.720\ A_{528}$	VGB	$2.62\ A_{515}$
BLE Powder	$1.43\ A_{538}$		

* Coupled color insoluble in methanol-hydrochloric acid. Equation is for sample coupled in methanol-hydrochloric acid and diluted with glacial acetic acid.

TABLE III

EQUATIONS FOR ANTIOXIDANTS CONTAINING PBNA REQUIRING ALTERNATE PROCEDURE

Antioxidant	Equation % antioxidant =	Antioxidant	Equation % antioxidant =
Agerite HIPAR	1.67 A_{534}	Neozone D	1.25 A_{534}
Agerite HP	2.47 A_{534}	PBNA	1.25 A_{534}
Agerite Powder	1.25 A_{534}	Thermoflex A	2.49 A_{534}
Akroflex CD	1.92 A_{534}	Thermoflex C	2.12 A_{534}

The factor 0.1 is used because of a ten ml aliquot which is taken from a 100 ml sample. If a 1.000 gram sample is always taken, then

$$\% \text{ Antioxidant} = 1000\ (AC) \tag{3}$$

The equations for the various antioxidants are given in Tables II and III.

The antioxidants for which the method has been found to be unsatisfactory are Agerite White, Antioxidant 4010, BXA, Eastozone 32, JZF (DPPD), OZO 88, Santoflex AW, Santoflex BX, Santoflex DD, Santoflex 35, Santoflex 75, Tenamine 2, Tenamine 30, Tonox, Tonox D, U.O.P. 88 and U.O.P. 288.

EXPERIMENTAL RESULTS

All of the antioxidants listed in Tables II and III conform with Beer's Law. Figure 10 shows this conformity for four of these antioxidants.

Results with stocks containing known amounts of Agerite Stalite, BLE-25 and PBNA are shown in Table IV. For all of these, known amounts of the antioxidant were milled into Synpol-1502 and the antioxidant content was checked by ultraviolet absorption analysis.

The method does not cover all the commercial amine antioxidants. However, the coverage is considerably greater than any of the methods previously reported. Further work would be required in order to take care of all the

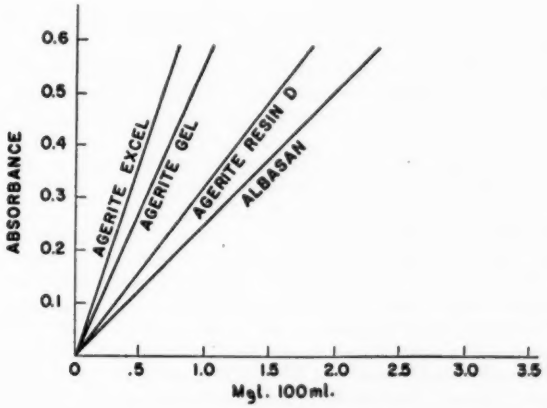


FIG. 10.—Conformity with Beer's Law.

TABLE IV

RESULTS OBTAINED WITH METHOD ON STOCKS CONTAINING KNOWN AMOUNTS OF ANTIOXIDANTS

Per cent present	Per cent found	Per cent error (relative)
	Agerite Stalite	
1.00	1.00	0.00
	1.00	0.00
0.58	0.58	0.00
	0.58	0.00
0.28	0.27	3.57
	0.27	3.57
0.16	0.16	0.00
	0.16	0.00
		Avg. 0.89%
	BLE-25	
0.92	0.93	1.08
	0.92	0.00
0.57	0.58	1.75
	0.58	1.75
0.30	0.29	3.33
	0.32	6.67
0.17	0.17	0.00
	0.17	0.00
		Avg. 1.84%
	PBNA	
0.94	0.94	0.00
	0.94	0.00
0.67	0.68	1.49
	0.67	0.00
0.36	0.36	0.00
	0.36	0.00
0.18	0.17	5.56
	0.17	5.56
		Avg. 1.58%

possible causes for the failure of the method. It might be well to discuss a few of these possibilities:

Mixtures of antioxidants.—If both antioxidants can be found in Table II, the spectrum usually indicates which antioxidants could be present. Synthetic mixtures can then be prepared and the spectrum of the coupled mixture determined.

Oxidized antioxidants.—Since oxidized antioxidants will couple differently depending upon the type of antioxidant and the extent of oxidation, the method will not work if much oxidation has taken place.

Strongly colored alcohol extract.—If the interference is mostly at the shorter wavelengths, 350 to 425 millimicrons, some correction can be made by coupling a ten ml aliquot and a five ml aliquot. Determine the absorption spectra of these solutions using a five ml aliquot (containing no coupling agent) diluted to 100 ml with methanol-hydrochloric acid as the solution in the blank cell. In this way most of the interference from other material can be eliminated. The difference between the spectrum of the coupled ten ml aliquot and the coupled five ml aliquot is taken as the correct spectrum for a coupled five ml aliquot. If this corrected spectrum matches one of the spectra in Figures 1 to 9, the

quantitative determination is made by multiplying by two the value found by using the equation for the antioxidant concerned. This takes care of the fact that a five ml rather than a ten ml aliquot is used.

SUMMARY

A method is described for the qualitative identification and quantitative estimation of many of the more common amine antioxidants. The method is comparatively simple and requires less than one-half man hour per determination. The method is accurate and precise. Analyses with known stocks showed an average error of less than 2% relative.

ACKNOWLEDGMENT

The author gratefully acknowledges the work of D. N. Pregler who carried out much of the experimental work described herein.

REFERENCES

[1] Bellamy, L. J., Lawrie, J. H. and Press, E. W. S., *Trans. Inst. Rubber Ind.* **23**, 15 (1947).
[2] Brock, M. J., and Louth, G. D., *Anal. Chem.* **27**, 1575 (1955).
[3] Budig, K. H., *Kautschuk u. Gummi* **1**, 177 (1948).
[4] Burenfield and Judy, *Anal. Chem.* **19**, 786 (1947).
[5] Craig and David, *Ind. Eng. Chem., Anal. Ed.* **9**, 56 (1937).
[6] Deal, A. J. A., *Trans. Inst. Rubber Ind.* **23**, 148 (1947).
[7] Hamazaki, F. J., *J. Soc. Rubber Ind. Japan* **23**, 302 (1950).
[8] Hively, R. A., et al., *Anal. Chem.* **27**, 100 (1955).
[9] Kawaguchi, T., et al., *J. Soc. Rubber Ind. Japan* **27** (1954).
[10] Koide, T., et al., *J. Soc. Rubber Ind.* **22**, 108 (1949).
[11] Koide, T., et al., *J. Soc. Rubber Ind.* **22**, 256 (1949).
[12] Mann, J., *Trans. Inst. Rubber Ind.* **27**, 232 (1951).
[13] Mensik, P., and Broulik, D., RUBBER CHEM. & TECHNOL. **29**, 647 (1956).
[14] Morita, E., *J. Soc. Rubber Ind. Japan* **26**, 259 (1953).
[15] Newell, J. E., Unpublished work (1951). Present address: Naugatuck Chemical Division, U. S. Rubber Company, Naugatuck, Connecticut.
[16] Parker, C. A., and Berriman, J. M., *Trans. Inst. Rubber Ind.* **28**, 279 (1952).
[17] Zijp, J. W. H., *Recueil* **75**, 1155 (1956).

THE INFRARED SPECTROSCOPIC IDENTIFICATION OF RUBBER BEFORE AND AFTER CURE TO THE SOFT AND HARD RUBBER STATES *

DIETER HUMMEL

ROBERT BOSCH, GMBH., STUTTGART, GERMANY

INTRODUCTION

The identification of raw rubber and vulcanizates can be made by physical and chemical methods; several of the known methods are assembled in the booklet by Frey[1]. Unfortunately, many physical properties of high polymers are not very specific, and chemical reactions with high polymers run very slowly at the best. Some of the difficulties are overcome by using certain physical values (density, swelling in different solvents), and simple chemical reactions (testing for heteroatoms) in tests for identification of an unknown sample. Now it has been shown that practically all technically useful varieties of rubber form characteristic products of pyrolysis, with which definite color reactions can be obtained. The familiar analytical instructions of Burchfield[2,3] are based on these observations.

The growth of infrared spectroscopy in the last fifteen years has also been helpful for the analysis of rubbers and gums. Barnes and coworkers[4,5] first reported on the IR-spectra of various types of rubber. These authors recommended a mixture of 5 parts *p*-cymene and 1 part xylene (mixed isomers) as solvent for the vulcanizates. They observed widespread spectral similarity between the raw rubber and a vulcanizate based on the same rubber, which had been degraded by a solvent. A few years later Dinsmore and Smith[6] reported on their extensive studies of the IR-spectroscopic analysis of natural and synthetic rubbers. They found difficulties in operating by the procedure given by Barnes and coworkers, and recommended *o*-dichlorobenzene as a fairly universal solvent. They worked out quantitative methods for natural rubber/GR-S mixtures and for Buna N.

Since the degradation of vulcanizates to a soluble stage in the usual organic solvents is a time consuming operation, the idea occurred of using the products of pyrolysis in the IR-spectroscopic identification of rubbers. Kruse and Wallace[7] subjected a great many high polymers to pyrolysis and examined the pyrolysates spectroscopically, after they were dissolved in carbon tetrachloride. Harms[8] reports on extensive studies on complex high polymer materials (plastics, rubbers, varnish materials). He did not use any solvent for the pyrolysis products, but examined spectroscopically the readily condensable materials, between rock salt disks.

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* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by W. D. Wolfe. This article appeared originally in *Kautschuk und Gummi*, Vol. 11, No. 7, WT 185–190 (1958). Part of the material in this article is included in the author's work, "Analyse von Kunststoffen, Lacken und Gummi", published by Carl Hanser Verlag, München, 1958. The present address of the author is Institut für physikalische Chemie und Kolloidchemie, Universität zu Köln, Köln, Germany.

DEGRADATION OF POLYMERS BY MILLING AND WITH SOLVENTS

In our laboratory, we worked with the procedure of Dinsmore and Smith. In this work, we found that vulcanizates dissolve physically in solvents only if they have been previously subjected to a more or less vigorous polymer breakdown, preferably by working on a mill. Individual vulcanizates respond in their own way to this treatment, hence the optimum conditions must be sought for each case. Usually a half hour working with heavy friction and at higher temperatures is satisfactory. Normally it is not possible to reduce a vulcanizate in this way to a sticky cohesive mass which will dissolve cold in the usual solvents, without the use of some regenerating agent. Prolonged boiling with *o*-dichlorobenzene (b.p. 170° C) further breaks vulcanizate bonds. At the same time a molecular degradation probably takes place with rupture of the bonds in the chain molecules, so that the polymer dissolves in the solvent to a low viscosity solution that can be readily handled.

Before milling, the vulcanizates were cut into thin strips and extracted for half of an hour with butanone in the manner described by Kress[9]. After milling, the degraded vulcanizates were in the form of crumbs or in weak sheets; they were allowed to swell in *o*-dichlorobenzene for some time at room temperature. The final boiling with *o*-dichlorobenzene was done on a sandbath, under

TABLE I

BEHAVIOR OF DIFFERENT TYPES OF SOFT RUBBER VULCANIZATES IN BOILING *o*-DICHLOROBENZENE

Soft rubber base	Natural rubber	Butyl rubber	Natural/ butyl mix	Buna S	Perbunan	Neoprene
Cooking time, hrs	2½	8	6	16	30	26
Amount dissolved, %	100	100	100	100	40	14

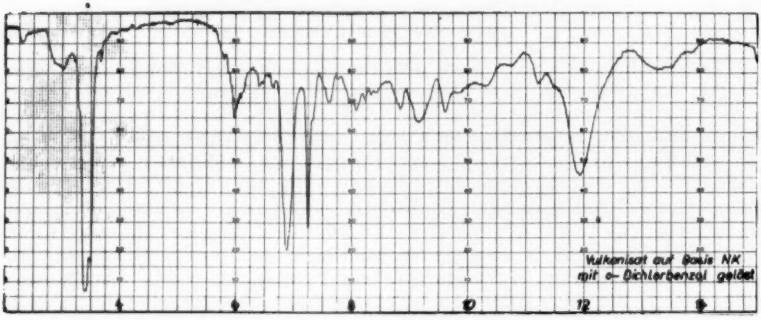
a nitrogen atmosphere; the mixture was stirred during the whole operation in order to prevent sticking. To eliminate pigments and fillers, we added a sufficient amount of Mikrofil-Filteraid to the solution, boiled briefly and then centrifuged at 4000 rpm. Particles of the vulcanizate were previously screened out on a copper screen. The *o*-dithlorobenzene was distilled off with the use of a water aspirator, admitting nitrogen through a capillary, to prevent oxidation of the polymer. The remaining syrupy solution was brushed on NaCl disks and the residual solvent removed in a vacuum oven.

The behavior of the different soft rubbers, which we studied, with boiling *o*-dichlorobenzene is given in Table I. Perbunan and neoprene vulcanizates did not dissolve in this solvent even with prolonged boiling.

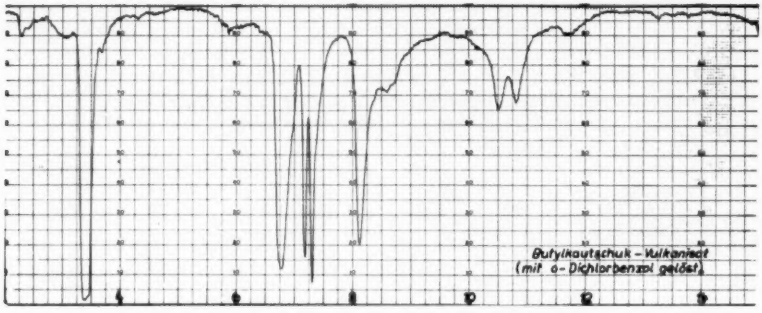
The partially degraded polymers recovered from these vulcanizates showed an extensive spectral similarity to the corresponding rubber types as shown in Figure 1.

POLYMER DEGRADATION BY PYROLYSIS

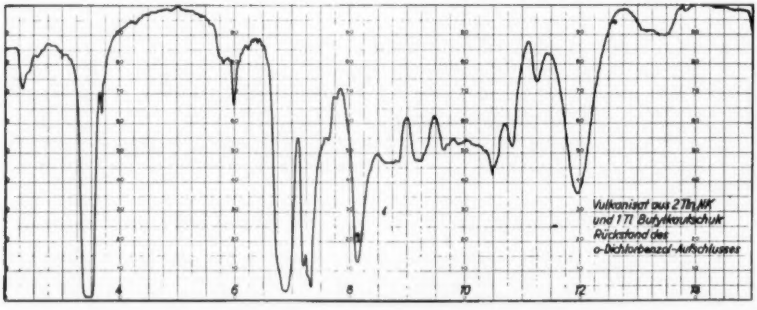
It is true that the above described method gave some excellent results, yet it is time consuming. We therefore sought to improve the more rapid method of complete degradation of the polymers by pyrolysis, so that it would match the method of careful degradation in reliability.



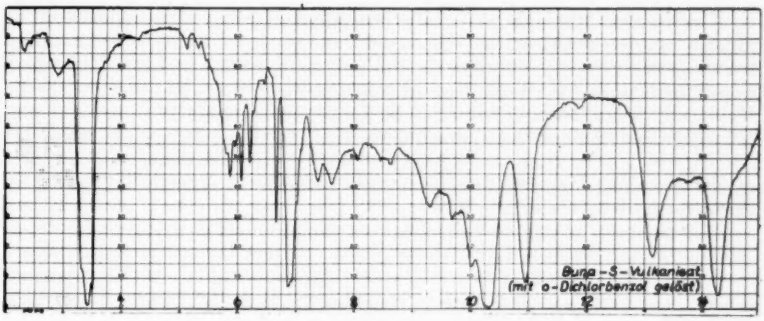
1-1. Natural rubber vulcanizate dissolved in *o*-dichlorobenzene.



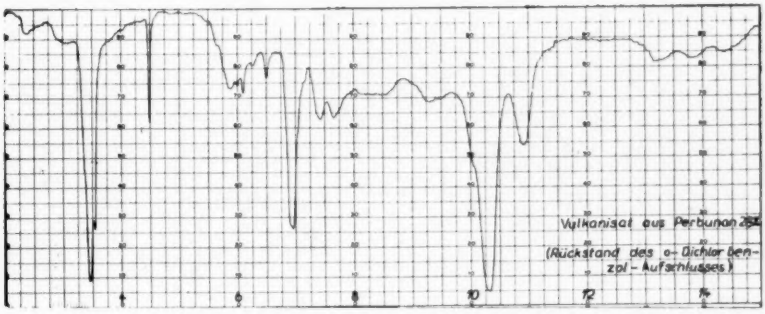
1-2. Butyl rubber vulcanizate dissolved in *o*-dichlorobenzene.



1-3. Vulcanizate of 2 parts natural plus 1 part butyl rubber. Residues from decomposition in *o*-dichlorobenzene.



1-4. Buna-S vulcanizate dissolved in *o*-dichlorobenzene.



1-5. Perbunan 2810 vulcanizate. Residue from decomposition with *o*-dichlorobenzene.



1-6. Neoprene vulcanizate dissolved in *o*-dichlorobenzene.

FIG. 1.—IR-spectra of rubber fractions from partly degraded vulcanizates.

The simplest pyrolysis mechanism is depolymerization with predominant or almost complete reformation of the monomers; examples of this behavior during pyrolysis are given by polystyrene and polymethylmethacrylate. This clean depolymerization with formation of the monomers does not occur with the technically useful sorts of rubber. In the pyrolysis products from these materials we find along with the monomers, whenever these do appear, molecular species which arise from transfers, cyclizations, condensations, and dehydrogenations. The course of these secondary processes is strongly influenced by pressure and temperature.

The monomer is the most significant of the products of pyrolysis for determining the starting material for the polymer. Hence, the conditions of pyrolysis should be so chosen as to produce the highest possible yield of monomer. Since the monomers used in various important varieties of rubber are low boiling liquids or gases under normal conditions (butadiene, isoprene, isobutylene,

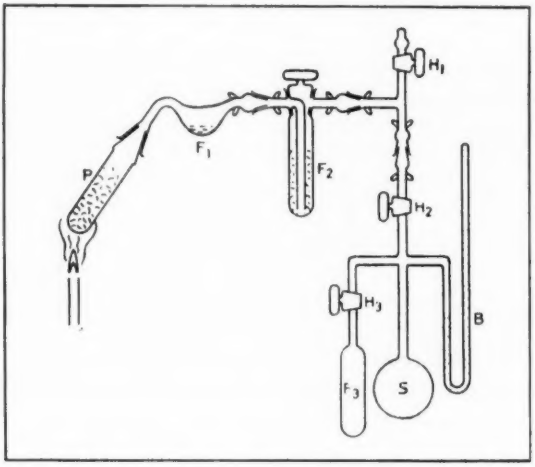


FIG. 2.—Pyrolysis apparatus.

2-chlorobutadiene-1,3), the gaseous products of pyrolysis should not be neglected in an analysis. In our work, we also found that other pyrolysis gases (HCN, CO_2, cyclic siloxanes) often gave worthwhile indications of the original composition of the polymer. The pyrolysis apparatus which we used in work under vacuum is shown in Figure 2.

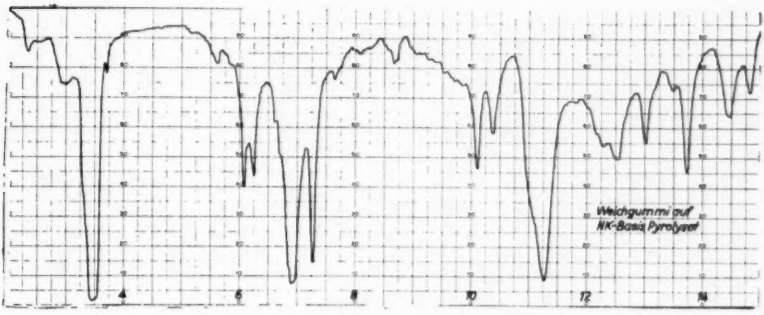
P is a quartz pyrolysis tube, in which the test material is placed for heating. This tube is attached to the rest of the apparatus by a connecting fitting which is lubricated with a highly graphited, high vacuum grease. F_1 is the first, pouch-shaped trap, in which the high boiling products of pyrolysis are collected. This trap may also be heated during a pyrolysis, in order to increase the depolymerization of the products from the pyrolytic degradation. F_2 is a trap with a removable absorption bulb. This can be filled with cotton or glass wool or similar material, so that neither mist nor smoke can get over to the gas cell. The gas cell which is used for the spectroscopic observations consists

of the spectroscopic cell S with rock salt windows, the trap F_3 and the short branched monometer B. F_3 is chilled with solid CO_2 or liquid air. When the gaseous products of pyrolysis have collected in F_3, the valves H_2 and H_3 are closed and the rest of the apparatus is brought to atmospheric pressure by opening H_1. The coolant is removed from F_3 and a chosen gas pressure is established in S by careful manipulation of valve H_3. For a 10 cm light path, a pressure in S of 50 mm of Hg is usually correct.

It has been found that, in the process of pyrolysis, it is advantageous to heat the tube P from the upper end down, and to carry out the decomposition quickly and completely. The product collected in F_1 and the degradation products, gaseous under ordinary conditions, which are trapped in F_3, are examined spectroscopically. The spectra which are obtained are compared with standard spectra which are obtained from pyrolysis products of known materials.

SOFT RUBBER

Vulcanizates of natural rubber.—The pryolysis of natural rubber and its vulcanizates, depending on temperature and pressure, gives rise to more or less

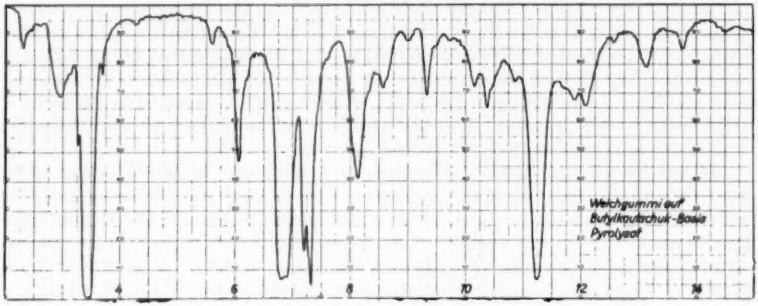


3-1. Natural based soft rubber, liquid pyrolysate.

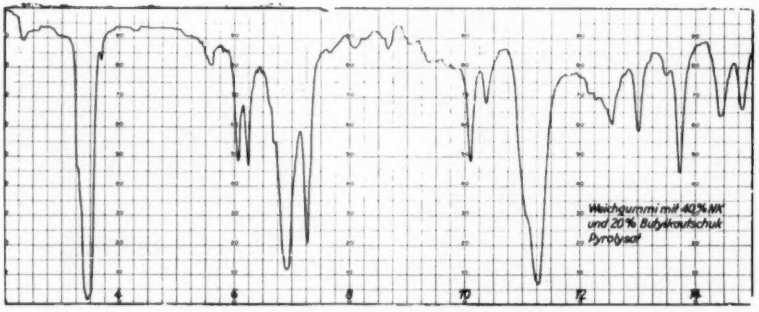
isoprene, oligomers of isoprene (mainly dipentene), other degradation products of an olefinic nature, and aromatic compounds. Figure 3-1 shows the spectrum of a pyrolysis product, liquid at room temperature, which was obtained from an ordinary soft rubber made with natural rubber. The intense absorption at 11.27 μ comes from the vinylidene groups which are found as end groups in isoprene:

$$\begin{array}{l} -C=CH_2 \\ \quad | \\ \quad CH_3 \end{array}$$

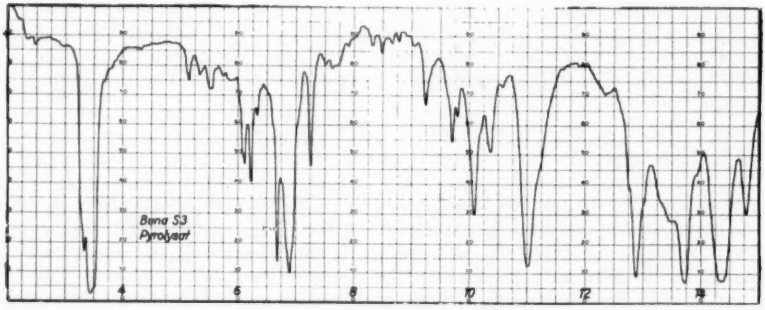
Absorptions at 10.1 μ and 11 μ are associated with vinyl groups which are also common to isoprene and its polymers: $-CH=CH_2$. A band at 10.38 μ probably comes from *trans* vinylene groups in the degradation products, which originate in secondary processes. The absorptions between 12 and 15 μ, together with the moderately strong band at 6.25 μ, are the result of aromatic groups. Conjugated olefinic double bonds can also play a part in the 6.25 μ



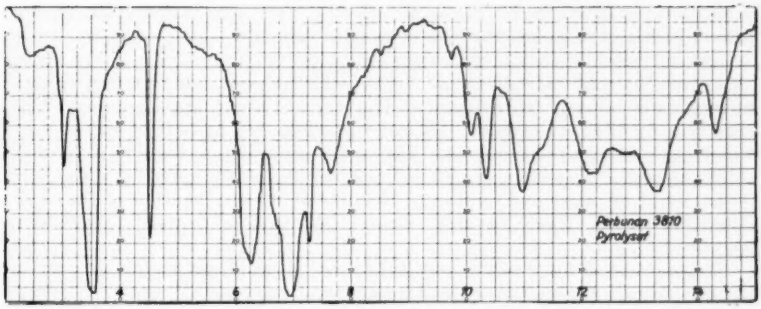
3-2. Butyl based soft rubber, liquid pyrolysate.



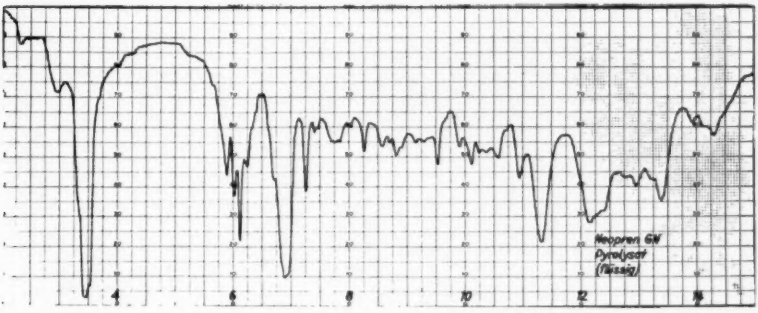
3-3. Soft rubber from 40% natural with 20% butyl, liquid pyrolysate.



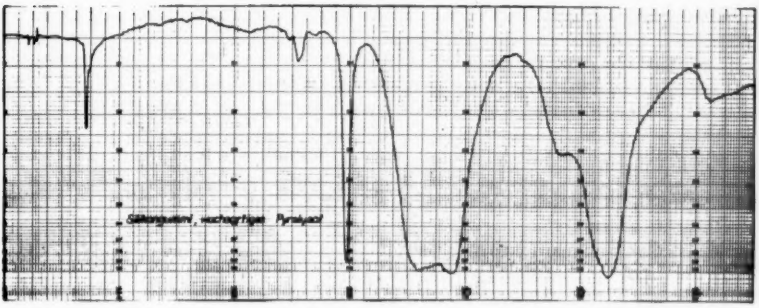
3-4. Buna S-3 soft rubber, liquid pyrolysate.



3-5. Perbunan 3810 soft rubber, liquid pyrolysate.



3-6. Neoprene GN soft rubber, liquid pyrolysate.



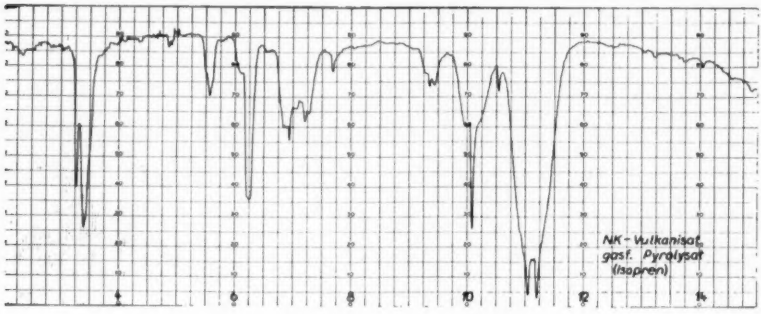
3-7. Silicone R 20 soft rubber, waxy pyrolysate.

FIG. 3.—IR-spectra of ordinarily liquid pyrolysates from various soft rubbers.

absorption; isolated double bonds absorb at 6.1 μ. The intense CH_3 absorption at 7.28 μ is also characteristic of natural rubber.

The mixture of substances in the pyrolysate just described is a very strong indication that natural rubber was the starting material, but its composition is not always accurately reproducible. The study of the pyrolysis gases provides certainty, for they consist mainly of isoprene when they come from vulcanizates which are based on polyisoprene. The isoprene spectrum, Figure 4-1, is characterized by the vinylidene absorption at 11 to 11.2 μ; the splitting of the bond is the result of molecular rotation. Because of the conjugation of the C=C double bond, the C=C valence vibration is displaced toward longer wave lengths at 6.25 μ.

Vulcanizates of butyl rubber.—Butyl rubber is composed mainly of polyisobutylene copolymerized with small amounts of isoprene or butadiene (about 1%). Figure 3-2 shows the spectrum of the pyrolysis products, liquid under normal conditions, which were derived from a butyl vulcanizate. Except for the weak absorptions between 12.5 and 15 μ, which are lacking in the spectrum of the pyrolysates of Oppanol 200, this corresponds to the spectrum of a ther-



4-1. Natural based soft rubber, gas (isoprene) pyrolysate.

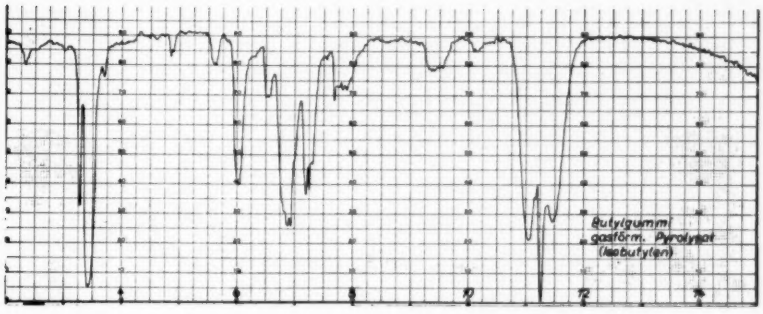
mally degraded polyisobutylene. The band at 11.25 μ is significant; it is to be correlated with the vinylidene group as it is in the case of natural rubber. The spectrum of the pyrolysis products from butyl rubber differs sharply from that of materials derived from natural rubber in their absorptions at 7.2 and 7.3 μ and at 8.15 μ, which arise from the isopropyl groups. Aromatic groups are not present.

As in the case of natural rubber, varying amounts of monomers, depending on the pyrolysis conditions, are derived from butyl rubber. Isobutylene makes up the largest proportion of the pyrolysis gases. Its spectrum, Figure 4-2, is quite characteristic, and like the spectrum of isoprene, it shows the absorption of the vinylidene groups between 11 and 11.5 μ. Since the isobutylene molecule is almost 20% lighter than the isoprene molecule and has an almost spherical form, the moment of inertia of isobutylene is less than that of isoprene; hence the rotation structures are farther apart (11.05 μ, 11.25 μ and 11.46 μ). The C=C vibration lies at the normal location of 6.03 μ. Asborptions by vinyl and vinylidene groups are absent.

Vulcanizates of natural rubber/butyl rubber compounds.—In the pyrolysis of the vulcanizate of a mixture of 2 parts natural rubber and 1 part butyl rubber, we were surprised to find that practically no oligomers of isobutylene were to be found in the pyrolysis products which were liquid under ordinary conditions. The spectrum of this liquid fraction, Figure 3-3, closely resembledt he spectrum of a natural rubber based vulcanizate, Figure 3-1. The pyrolysis gases showed in their spectrum, Figure 4-3, as a mixture of isoprene and isobutylene along with small amounts of other compounds of uncertain composition.

When the ordinarily liquid pyrolysate of an unknown rubber sample gives indications of nothing but natural rubber, it will still have to be shown whether or not the pyrolysis gases contain isobutylene.

Vulcanizates of Buna S.—In the pyrolysis of Buna S types and vulcanizates prepared therefrom the characteristic degradation products are styrene and butadiene monomers together with oligomers of homo- and copolymers. Most of the styrene is found in the liquid fraction; the spectrum of this pyrolysate, Figure 3-4, will therefore be characterized by the bands for monomeric styrene



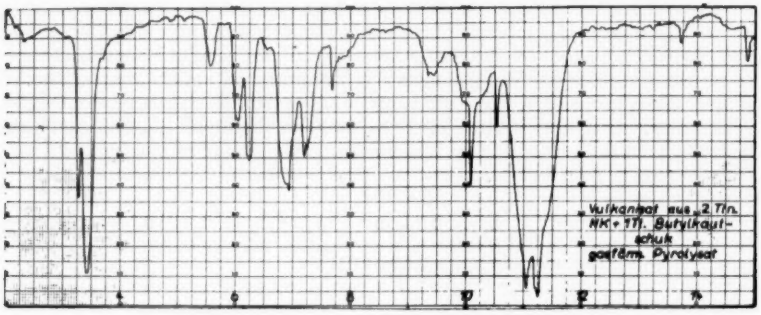
4-2. Butyl based soft rubber, gas (isobutylene) pyrolysate.

at 10.1, 11.0, 12.9 and 14.35 μ. In addition, bands are also found for a number of other components which are also characteristic of the original copolymer.

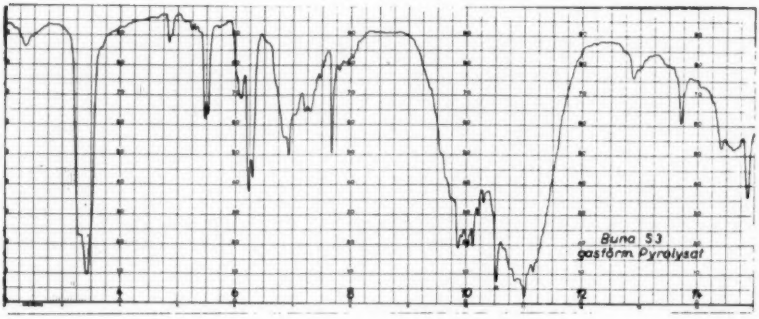
There is practically no styrene absorption in the spectrum of the pyrolysate which is gaseous under normal conditions, Figure 4-4. The very intensive absorptions which overshadow all the rest of the spectrum and which show at 10 μ and 11 μ belong to monomeric butadiene and oligomers from butadiene which have end-vinyl groups. Indicative also of butadiene are the weak to moderately strong double bands at 5.5 μ (about 1820 cm^{-1}) which are probably the first overtone (2×910 cm^{-1}) of the intense absorption at 11 μ. The pointed band at 10.54 μ comes probably from the ethylene content.

Vulcanizates from Perbunan N.—Whenever nitrogen is found in an unknown rubber, there is usually an acrylonitrile copolymer present. The appearance of nitrile-, imine-, and amine-like compounds in the degradation products is characteristic of the pyrolysis of such materials; ammonia is also usually found.

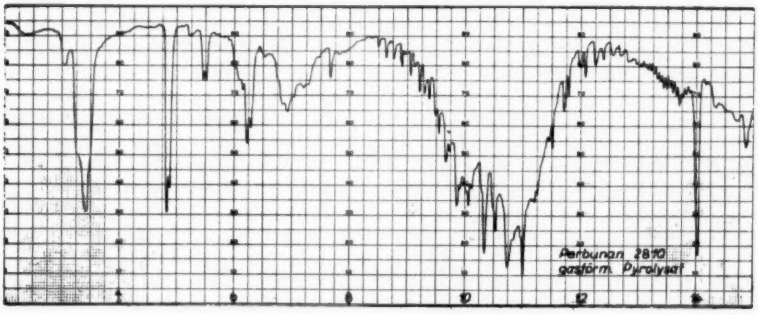
The spectrum of the ordinarily liquid fraction of the products of pyrolysis of Perbunan N 3810 (a copolymer of 62% butadiene and 38% acrylonitrile) is



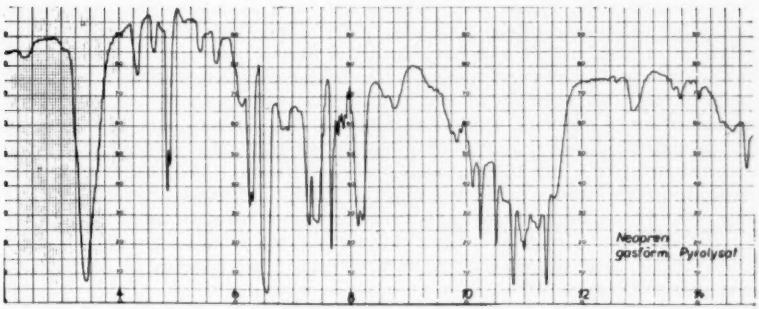
4-3. Soft rubber from 2 parts natural plus 1 part butyl, gaseous pyrolysate.



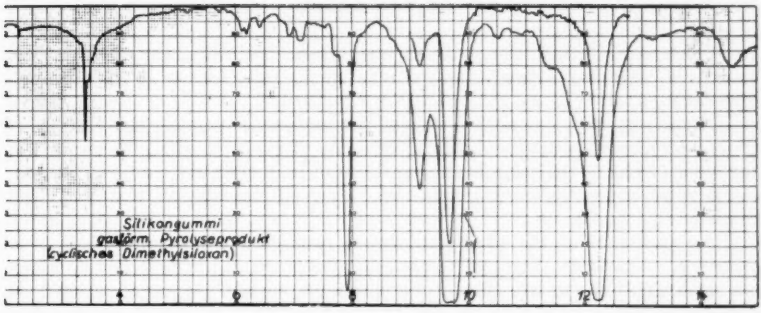
4-4. Buna S-3 soft rubber, gaseous pyrolysate.



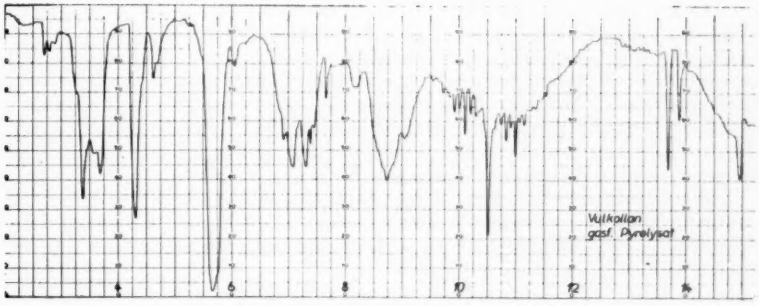
4-5. Perbunan 2810-soft rubber, gaseous pyrolysate.



4-6. Neoprene soft rubber, gaseous pyrolysate.



4-7. Silicone R 20 soft rubber, gaseous pyrolysates (cyclic dimethylsiloxanes).



4-8. Soft Vulkollan, gaseous pyrolysate.

FIG. 4.—IR-Spectra of normally gaseous pyrolysates from various soft rubbers.

very characteristic, Figure 3-5. The sharp band at 4.52 μ (C≡N valence vibration) belongs to nitrile products, which apparently are oligomers of copolymers of acrylonitrile and butadiene. A narrow, moderately strong N-H valence vibration shows at 3.02 μ, which indicates an imino or mono substituted amino group. A fairly broad and intense absorption at 6.25 μ is caused by superposition of aromatic ring vibrations and δ_{NH} vibrations. The band at 7.28 μ indicates methyl groups of secondary origin. The moderately strong absorptions at 10.1 and 10.98 μ belong to vinyl groups. A band at 10.35 μ is associated with intermediate *trans* vinylene groups. The absorptions between 12 μ and 15 μ apparently belong to aromatic groups from secondary reactions.

The lack of acrylonitrile in the pyrolysis products from a copolymer of that compound is quite remarkable. The spectrum of the gaseous products from pyrolysis of Perbunan 2810, Figure 4-5, is characterized by the absorptions by ammonia, monomeric butadiene, and hydrocyanic acid. Butadiene shows up in the double band at 5.5 μ and a number of absorptions between 10 and 11 μ. The absorptions by ammonia coincide partly with those by butadiene; especially indicative of ammonia are the absorption at 10.73 μ and the paired absorptions at about 11.25 μ, 11.5 μ, 11.75 μ and between 9 and 10 μ. The intense, very sharp band at 14 μ belongs to hydrocyanic acid. The many weak bands between 13 and 14 μ are rotation spectra of the HCN molecule.

We were not able to ascertain the significance for the absorption band at about 4.85 μ; it also occurs in the spectrum of the gases formed in the pyrolysis of neoprene.

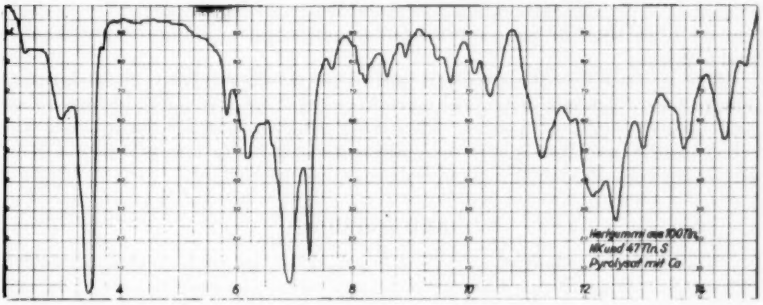
Vulcanizates of neoprene.—In the pyrolysis of poly-2-chlorobutadiene (polychloroprene, neoprene types, Perbunan C types) and its vulcanizates, the chief products are degradation products of low volatility, and, in addition, a very small amount of gaseous material. Since HCl is split off, the pyrolysate is acidic.

The spectrum of the ordinarily liquid product from the pyrolysis of a neoprene vulcanizate, Figure 3-6, actually shows no absorption bands which are entirely characteristic for the original polymer. The large number of bands however is significant enough to make the identifiction of an unknown product possible. The band at 7.28 μ indicates CH_3 group of secondary origin. The intense absorptions in the long wave region, together with the ring vibrations at 6.25 μ, indicate aromatics which come from cyclization reactions. The band at 11.32 μ is evidently indicative of a γ vibration of vinylidene groups.

The spectrum of the ordinarily gaseous fraction, Figure 4-6, shows many features which are common to the spectrum of 2-chlorobutadiene. The sharp bands at 10.26 μ and 10.84 μ are evidently γ vibrations of the H atoms of vinyl groups. The displacement from the normal position is ascribed to the neighboring chlorine. The very narrow absorption band at 11.4 μ is likewise the result of the γ vibration of the hydrogen atom of the vinylidene group; the red displacement here is also connected with the neighboring chlorine atom. The strong absorption at about 6.55 μ is possibly a δ_{CH_2} vibration.

Silicone rubbers.—This type of vulcanizate is easy to identify by its silicon content and by the white smoke which forms when it burns. Confusion may arise from these simple tests, because there are other vulcanizates which are loaded with SiO_2.

A valuable characteristic, from an analytical viewpoint, of the dialkyl—or aralkyl—polysiloxanes which occur in technical products (Silicones) is found in the fact that they are split at high temperatures, relatively smoothly, into linear or cyclic, low molecular weight, volatile siloxanes. If pyrolysis is con-



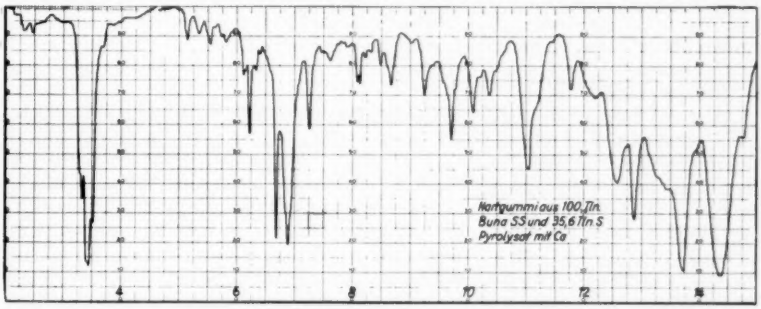
5-1. Hard rubber from 100 parts natural plus 47 parts sulfur, liquid pyrolysate with Ca.

ducted in the absence of air, a silicone rubber can be pretty effectively separated from filling materials.

By heating a vulcanizate based on Silikon R 20, we obtained a yellowish waxlike product of pyrolysis which formed an icelike pattern on the walls of the tube and which melted to a mobile liquid at a little above room temperature.

Silicones show a very characteristic spectrum with very intense absorption bands; for this reason polysiloxanes, even in mixtures, are usually very easy to identify. The pyrolysis product mentioned above was composed of low-molecular weight siloxanes. Its spectrum, Figure 3-7, resembled that of polydimethyl siloxane. The band at 7.95 μ is a vibration from internal $Si(CH_3)_2$ groups. The broad absorption between 9 and 10 μ comes from Si—O valence vibrations. The shoulder at 11.6 μ arises from $Si(CH_3)_3$ end groups. The band at 12.5 μ is a Si—C valence vibration from internal $Si(CH_3)_2$ groups. A needle shaped sublimate had formed in the gas cell. The spectrum of the gaseous product, Figure 4-7, is very characteristic and corresponds to that of a cyclic dimethylsiloxane oligomer. Characteristic of cyclic siloxanes is the absence of any absorption at 13.27 μ, which is correlated with $Si(CH_3)_3$ end groups.

Vulkollan.—Chemically, Vulkollan is a polyester-urethane based on an adipic acid-glycol polyester with alcoholic end groups and naphthalene-1,5-diiso-



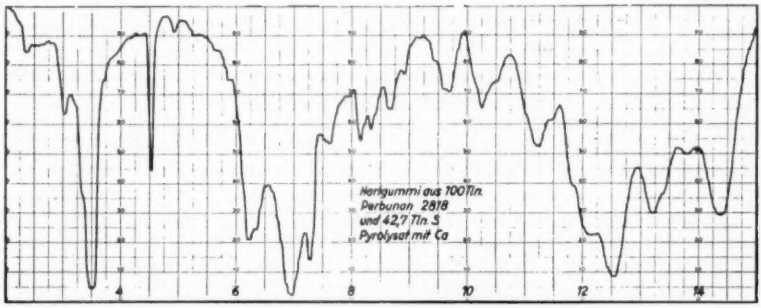
5-2. Hard rubber from 100 parts Buna S plus 35.6 parts sulfur, liquid pyrolysate with Ca.

cyanate. The rubbery product, in the absence of softeners and fillers, is well known for its tear and abrasion resistance and its easy saponification with acids and alkalies.

The spectrum of the pyrolysis gases of Vulkollan is very characteristic, Figure 4-8. The band with the highest intensity is at 5.65 μ and belongs to an unknown carbonyl compound. Urethanes generate CO_2 by decarboxylation when heated, and this is shown by absorptions at 4.3 μ and at 14.9 μ. The bands between 10 and 11 μ come from an ethylene content.

HARD RUBBERS

Hard rubber (Ebonite) can be recognized by its high content of sulfur (25–40%). Only Hypalon compounds may contain less sulfur. The positive identification of the rubber basis of a hard rubber offers difficulties because of the pronounced crosslinking of the polymer and the high content of foreign materials. We found, however, that hard rubber can be identified by its pyrolysis products. In order to reduce to a minimum all sulfur compounds and free sulfur in the products of pyrolysis, we mixed the finely divided hard rubber



5-3. Hard rubber from 100 parts Perbunan 2818 plus 42.7 parts sulfur, liquid pyrolysate with Ca.

FIG. 5.—IR-spectra of the normally liquid pyrolysates of various hard rubbers.

sample with an excess of zinc dust or finely powdered calcium, or a mixture of the two. The spectrum of the ordinarily liquid product of pyrolysis is usually quite characteristic of the rubber basis of the hard rubber. In certain cases it is recommended that the spectrum of the gaseous decomposition products should also be examined.

Natural rubber vulcanizates.—Olefinic and aromatic hydrocarbons are the chief products of pyrolysis of an ebonite when mixed with Zn or Ca; sulfur bearing compounds are also detected (odor). The spectrum of the ordinarily liquid product of pyrolysis, Figure 5-1, is similar in certain respects to the spectrum of the liquid obtained by pyrolysis of soft natural rubber, Figure 3-1. Appreciably more aromatics are obtained from the hard rubber (absorptions between 12 and 15 μ), while the content of vinylidene groups is much reduced (bands at 11.27 μ). The composition and accompanying spectral picture of the liquid product of pyrolysis is quite reproducible, even when the sulfur content of the hard rubber varies within certain limits.

The gaseous products of pyrolysis obtained in our experiments with hard rubber based on natural rubber were not characteristic, and contained no isoprene.

Buna S vulcanizates.—Pyrolysis of hard rubber based on Buna S yields chiefly liquid products. These liquids have very nearly the same spectra as shown by the liquid products of pyrolysis of soft Buna S rubbers, compare Figure 5-2 with Figure 3-4. Only the intensities of some of the bands have changed.

Vulcanizates of Perbunan N.—When nitrogen is found in a hard rubber, the material probably contains an acrylonitrile copolymer. The pyrolysis is conducted under vacuum and in the presence of the metal powders, and both the liquid and gaseous products of decomposition are examined spectroscopically.

The spectrum of the liquid product obtained from the pyrolysis of one of the Perbunan N based hard rubbers, Figure 5-3, shows the nitrile band at 4.53 μ. The absorptions between 12 μ and 15 μ are more intense than the comparable bands in the spectrum of the products of pyrolysis of the soft rubber from Perbunan N, and moreover the intensities of the bands relative to each other are changed: more aromatic compounds of different substitution types are derived from the hard rubber.

The spectrum of the normally gaseous products was like that of the analogous products from solft rubber based on Perbunan N, except for an additional intense band at 12.95 μ, the significance of which is not known by us.

SUMMARY

The IR-spectroscopic identification of soft rubbers may be made by:

1. Breaking down the vulcanizate on a mill followed by boiling with *o*-dichlorobenzene and then the spectroscopic examination of the polymer recovered from the solution.

2. Thermal degradation of the vulcanizates followed by spectroscopic examination of the liquid and gaseous products of pyrolysis. The rubber base of hard rubbers is determined by spectroscopic examination of the materials obtained by thermal degradation of mixtures of the hard rubbers with zinc dust or powdered calcium.

ACKNOWLEDGMENT

I wish to thank Hannelore Fuchs for her zealous cooperation.

REFERENCES

[1] Frey, H. E., "Methoden zur Chemischen Analyse von Gummimischungen," Springer Verlag, Berlin-Göttingen-Heidelberg, 1953.
[2] Burchfield, H. P., *Ind. Eng. Chem., Anal. Ed.* **16**, 424 (1944).
[3] *Ibid.* **17**, 806 (1945).
[4] Barnes, R. B. and coworkers, *Ind. Eng. Chem., Anal. Ed.* **15**, 83 (1943).
[5] *Ibid.* **16**, 9, 486 (1944).
[6] Dinsmore, H. L. and Smith, D. C. *Anal. Chem.* **20**, 11 (1948).
[7] Kruse, P. F. and Wallace, W. B., *Anal. Chem.* **24**, 2015 (1952); **25**, 1156 (1953).
[8] Harms, D. L., *Anal. Chem.* **25**, 1140 (1953).
[9] Kress, K. E., *Rubber World* **134**, 709 (1956).

BOND STRENGTH AT THE CORD-IMPREGNANT (ADHESIVE)-RUBBER BOUNDARY LAYER *

R. V. Uzina and M. S. Dostyan

The casing construction studied here comprises cord layers-adhesive layer-rubber (Figure 1).

Owing to the action of external forces and internal tensions, while the cover is in service, separation may occur. Separation takes three forms: (1) the adhesion type, i.e., when the adhesion becomes less than the cohesion of the bonded materials; (2) the cohesion type, when the adhesion is greater than the cohesion of the bonded materials; and (3) the combined type when the adhesion approaches the cohesion. In order to eliminate adhesion type separation, it is necessary to increase the bond strength of the system. This can be done by three methods: (1) changing the type of cord; (2) using impregnating compositions; and (3) changing the rubber compound.

The type of cord has a marked effect on the bond strength. For example cotton cord results in considerably greater bond strength value than artificial or synthetic fibers. The composition of the rubber compound also shows a marked effect on the strength of bonding with cord. The introduction of a series of plasticizers into the mix results in a fall in the strength of the rubber/cord bonds, and the use of active fillers causes the strength to increase. The effect of cord type and the composition of the casing rubber on the bond

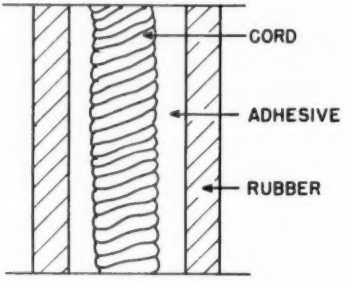


Fig. 1.

strength in the construction studied will be the subject of a separate investigation. The present report deals with the effect of the composition of the impregnating layer on the strength of the bond between the impregnated cord and the rubber.

* Prochnost' Svyazi na Poverkhnosti Razdela Kord-Propitochnyĭ Sloĭ-Rezina. Translation prepared by R. J. Moseley from '*Prochnost' Svyazi mezhdu Elementami Rezino-Tkanevykh Mnogosloĭnykh Izdeliĭ*. . . , VKhO im D. I. Mendeleeva Conference, Dec. 1954, pages 98–117.

As far as adhesion phenomena are concerned, and particularly in the field of impregnating compositions (adhesives), most of the work is of an empirical nature. Up to the present time there have been few attempts to arrive at a selection of adhesives on theoretical grounds.

The impregnating compositions used can be grouped as follows: (1) Latex with albuminous substances (casein, albumen, etc.)[1–4]; (2) Latex-resorcinol-formaldehyde compositions[1,2,5,6]; (3) Latex with casein and reclaim dispersions[1,2,6]; and (4) Synthetic resins[1–4].

The impregnating compositions used are based mainly on natural or synthetic latexes. Somes of the adhesives derived from the synthetic resins are based on polyisocyanates. The use of cements of this kind is limited by their harmful qualities, inflammability and lack of stability.

Reference (8) fills in some gaps in adhesion theory. However the nature of the bond in a complex triple system, to which cord/impregnating layer/rubber belongs, has been little studied theoretically up to the present time.

The purpose of this work is to explain the main requirements for working out the specification for impregnant compositions based on latex dispersions which will increase the strength of the bond in the system cord/rubber. For this purpose the effect of the following factors on the strength of the bond in this system have been studied:

1. The colloid-chemical properties of impregnating compositions.
2. The character of the surface.
3. The chemical composition of the adhesive.
4. The physico mechanical properties of the adhesive films.

EFFECT OF COLLOID–CHEMICAL PROPERTIES OF CHEMICAL COMPOSITIONS

The colloid-chemical properties of latex and impregnated compositions have up to the present been given little attention. This is partly due to the fact that the problem of impregnation is basically one of deep penetration of the compositions into textiles or cord. Voyutskiĭ and his colleagues[9–12] established that the properties of latexes such as particle size, viscosity, pH, surface tension, absorption stability, do not noticeably affect the impregnation properties.

TABLE I

EFFECT OF SURFACE TENSION OF LATEXES ON DEPTH OF IMPREGNATION AND BOND STRENGTH OF IMPREGNATED CORD TO RUBBER

Latex sample No.	Surface tension, dynes/cm	pH	Viscosity (centipoises)	Bond strength determined by stripping, kg			Depth of impregnation by micro-photography of sections		
				Viscose	Perlon	Cotton	Viscose	Perlon	Cotton
4	33.5	10.9	4.9	99.0	117.0	112.0	Insufficient flow between threads of 2nd ply	Extensive flow between fibers	Surface deposition
5	64.0	10.3	4.9	106.0	115.0	114.0	Insufficient flow between threads of 2nd ply	Extensive flow between fibers	Surface deposition

In order to study the impregnation properties of latex dispersions some investigators have made use of wetting agents, but the increased wetting capacity leads to a fall in bond strength[1,13].

The question as to whether thorough wetting of the cord by the impregnating composition, leading to deep impregnation, is necessary, has not been finally established up to the present time.

Our work has shown that a series of colloid-chemical characteristics of latex and impregnating compositions which were formerly considered to have considerable bearing on the impregnation of cord and textiles, do not have a direct influence either on deep impregnation or on the strength of the impregnating bond between cord and rubber (Table I)[14]. Thus the surface tension, like the viscosity and the pH value, does not affect deep cord penetration and bond strength with rubber. The depth of penetration of the cord also shows no direct influence on the bond strength with the rubber.

The basic colloid-chemical properties of latex, influencing its application as an impregnating composition, are its resistance to the action of water, to the introduction of various ingredients, to mechanical agitation and to temperature. These characteristics determine the suitability of latex for preparing impregnating compositions. Thus, example No. 1 (Table II) is not suitable for such a

TABLE II

COLLOID–CHEMICAL CHARACTERISTICS OF LATEXES

Latex sample No.	Conc., %	Surface tension, dynes/cm	Wetting angle	Viscosity, cp	pH	Limit of dilution		Gelling temperature, °C
						Factory water	Distilled water	
1	30.0	38.0	38°25′	13.0	11.5	Does not withstand dilution		30
2	30.0	37.0	38°30′	7.1	11.0	1:20	1:100	15
3	40.0	36.0	38°	7.35	10.9	Above 1:100	Above 1:100	12
4	21.5	33.5	—	4.9	10.9	Above 1:100	Above 1:100	Below 0

purpose as it does not withstand the action of water and passes to a gelatinous condition at room temperature.

The best type of latex for preparing impregnating compositions appears to be sample No. 4.

From the literature and our own investigations it follows that it is not the depth of penetration but the amount of impregnating material deposited on the cord that directly influences the bond strength with rubber. The amount of deposited substances is connected basically with the concentration of the impregnating material and with a number of technological factors related to the impregnating process (pressure, time of contact, speed, etc.)

On the question of the influence of the amount of deposited substance on bond strength and the quality of rubber-textile articles, contrary opinions exist. Some investigators consider that the greater the quantity deposited on the cord, the higher the bond strength. But a large number of authors believe that increasing the concentration above 10% and the amount deposited above 10–12% is undesirable[1–3,15].

Thus, Murphy and others[15] carried out work to establish a relationship between the amount of deposited substance on the cord, the adhesion and the

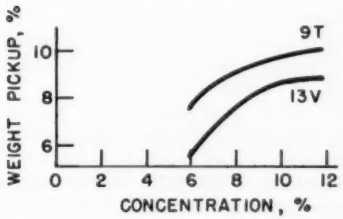


FIG. 2.—Increase of weight of cord due to penetration in relation to concentration of composition 50-u.

durability of tires in service. Increased adhesion per unit thread of cord at the expense of increased deposition of the impregnating material did not give good cover properties in service.

Our experimental data are in agreement with the opinions of a large number of investigators and show (Figures 2–4) that increasing the concentration of the impregnating substance above 9% leads to an insignificant increase in the amount of the deposited material and bond strength. Decreasing the concentration below 8% causes a sharp fall in the amount deposited and reduces the bond strength.

On the basis of the literature surveyed and our own experimental data it is possible to draw the following conclusions about the effect of colloid-chemical properties of latexes and impregnating compositions:

1. A variety of colloid-chemical properties of latexes and impregnating compositions show no effect on the strength of an impregnated cord/rubber bond (surface tension, angle of wetting, pH, depth of penetration);

2. The basic colloid-chemical characteristics, to which latex and impregnating compositions based on it must conform, are: stability to repeated dilution, mechanical and temperature effects, introduction of ingredients (albumen, resins, fillers), and the creation of conditions under which the amount deposited on the cord will not fall below 8 or above 12%.

EFFECT OF NATURE OF SURFACE

In studying bond strength of rubber/cord, careful attention must be paid to the influence of the cord surface. Many investigators consider that the bond strength of rubber with cord depends primarily on the quantity of cord fibers

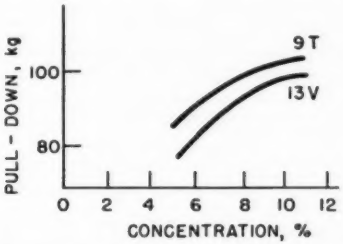


FIG. 3.—Stability of bond under static test of impregnated cord in relation to concentration of composition 50-u.

embedded in the rubber, and not on the structure of the cord itself[2,4,5,7,16–18]. The low bond strength of natural and synthetic fibers is explained by the fact that the fibers possess a smooth and not a teased-up surface, in contradistinction to the teased-up surface of cotton.

Borroff and others[17] carried out experiments to explain the effect of mechanical factors on bond strength. For this purpose they determined the bond strength of textiles from staple fiber (viscose, acetate silk, nylon, etc.) and textiles from continuous threads of the same fibers, using vulcanizates based on natural rubber and polar synthetic rubber. The highest strength is shown by threads from staple fiber and the poorest strength of all from acetate silk. From this the authors concluded that mechanical factors predominated over intermolecular interaction in bond strength. Staple fiber lowers the physico mechanical properties of the cord, and many investigators[7] have not found that it produces any increase in bond strength. Thus Finlayson expressed the opinion that the basic difference in the value of the adhesion of cotton and viscose lay in the smoothness of the viscose threads themselves due to the presence of a much rounder section than in cotton, which reduces the active surface contact between cord and rubber.

From our data in Table III it may be seen that viscose cord scoured and impregnated shows lower bond strength values than cotton cord despite its higher gage.

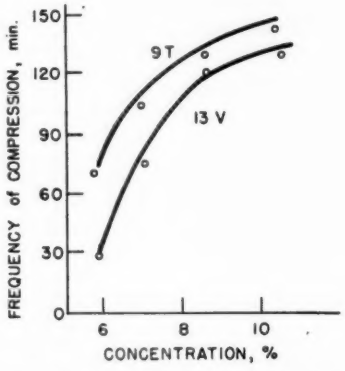


FIG. 4.—Bond strength under rapid compression (cord impregnated with rubber based on SKB) in relation to concentration 50-u.

TABLE III

BOND STRENGTH OF COTTON AND VISCOSE CORD WITH RUBBER BASED ON SKB

CORD	Bond strength between unit thread of cord and rubber		Bond strength of standard rubber-textile specimens	
	Pull-down, kg	Flexing time, min	Repeated flexing, 1000's of cycles	Repeated shear, cycles
Unimpregnated cotton	65.0	10	519	216
Unimpregnated viscose	45.5	4	200	166
Impregnated cotton	110.0	360	2142	450
Impregnated viscose	105.0	220	1800	382

TABLE IV

EFFECT OF THE NATURE OF THE SURFACE OF IMPREGNATED VISCOSE CORD ON BOND STRENGTH WITH RUBBER SKB

Impregnating composition	Bond strength: Pulldown, kg	Bond strength: Repeated compression, min	Bond strength: Repeated flexing, cycles	Type of breakdown	Cord surface
50-u	95.0–105.0	180–300	300–500	Adhesion at surface of separation between impregnating material/rubber	Smooth
30-DS	112.5	500	780	Cohesion at rubber	Loosened, like a comb

Viscose cord impregnated with a series of compositions 50-u[14] has a smooth surface. The introduction of fine black dispersions into the impregnating substance causes a disintegration of the viscose cord surface. There is then a marked increase of bond strength between impregnated cord and rubber (Table IV). (Figures 5 and 6 in the original illustrated this effect but were too indistinct to permit reproduction.)

The increased strength of the cotton cord bond compared with cord from artificial or synthetic fibers is explained by the greater roughness of the surface of the former. Therefore any process which will increase the surface of artificial or synthetic fibers will lead to greater bond strength.

EFFECT OF CHEMICAL COMPOSITION OF ADHESIVE

Most of the recent work on the rubber/textile system shows that the adhesion between organic polymers is a function mainly of the intermolecular and chemical interaction between the different groups in the adhesive surface. Attempts have been made to explain adhesion phenomena on the basis of polarity[7,16,17,19–21]. It has been suggested that such polar groups[22] as NH_2, OH, etc., might be introduced into impregnating compositions. In a similar way we can explain the increase in bond strength of impregnated cord by the use of resinous materials based on polyisocyanates[23,25] and phenylenediamine resins[26].

In recent years much attention has been given to the importance of electrical forces in adhesion[8,20,27]. Deryagin and Krotova[8] suggested and worked out an electrical theory of adhesive layers. The authors showed that in pulling down a layer work is done of the order of 10^5–10^6 ergs/cm^2 and that the specific work of adhesion depends on the speed of separation, increasing with it. These facts cannot be explained merely on the basis of the molecular or chemical nature of adhesion, as the work of separation exceeds the work needed to overcome the molecular or chemical forces. The authors consider that the chief role in the work of tearing is played by the electrical forces.

The essentials of the electrical theory of adhesion are that when contact is broken between two different surfaces a dual electrical layer of opposite charges is formed. This explains the high value for the work of separation (10^5–10^6 ergs/cm^2).

The authors of the electrical theory have examined the process of separation of this dual electrical layer when tearing occurs, and also the discharge leading

TABLE V

BOND STRENGTH IN RELATION TO COMPONENTS OF IMPREGNATING SUBSTANCES

Components of impregnating substances	Cotton cord (9T)			Viscose cord (7B)		
	Pull-down, kg	Repeated compression, min	Repeated bending, 1000's of cycles	Pull-down, kg	Repeated compression, min	Repeated bending 1000's of cycles
Impregnated cord	65.0	10	519	30.0	3	270
Latex	60.0	4	—	28.0	1	—
Latex with phenol alcohol	75.0	30	—	40.0	5	—
Latex with casein	95.0	40	—	60.0	15	—
Latex with casein and phenol alcohol	110.0	60	1000	85.0	35	1410
Latex with casein, phenol alcohol and accelerator groups	130.0	360	2142	96.0	120	3160

to the dissipation of this layer. Nothing has yet been worked out by these authors to explain this action on a scientifice basis.

The effect of polar substances on adhesion of the systems studied is confirmed by the fact that synthetic and natural latexes, according to our data, without the addition of albumen and resins (polar substances) do not increase the bond strength between impregnated cord and rubber.

From Table V it is evident that the introduction of formaldehyde resins, casein and accelerator groups, leads to an increase of the bond strength.

We will deal in detail with the effect of each of the added components to latex on the bond strength of the system cord-impregnating layer/rubber.

INTRODUCTION OF SYNTHETIC RESINS

The ingredients most often added to latex to make impregnating compositions are resorcinol formaldehyde resins[1,2,5,6]. The basic requirement for such resins, introduced into latex, is their solubility in water.

We have used, besides resorcinol formaldehyde resins, phenol formaldehyde resins, which are also water soluble.

The use in latex of phenol- and resorcinol-formaldehyde resins containing polar hydroxyl groups in the *ortho* and *meta* positions leads to an increase in bond strength (Figure 7). This is especially the case with resorcinol formaldehyde resins.

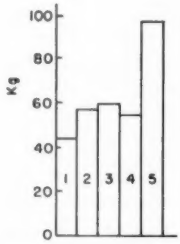


FIG. 7.—Effect of formaldehyde resins on bond strength of viscose cord with rubber, estimated by the method of pulling down unit threads: *1*. Latex; *2*. Latex +10 parts by weight phenol formaldehyde resin; *3*. Latex +15 parts by weight phenol formaldehyde resin; *4*. Latex +20 parts by weight phenol formaldehyde resin; *5*. Latex +20 parts by weight resorcinol formaldehyde resin.

TABLE VI

EFFECT OF INTRODUCING RESINS INTO LATEX ON THE BOND STRENGTH OF THE SYSTEM IMPREGNATING LAYER/RUBBER SKB

Characteristics of the system impregnating layer/rubber	Static separation, kg/cm	
	Before heating	After heating
Latex SKB	0.8	0.36
Latex + 10 parts by weight phenol formaldehyde resin-SKB	1.2	0.53
Latex + 20 parts by weight resorcinol formaldehyde resin-SKB	1.5	0.62

There is an opinion that the use in impregnating compositions of polar resins leads to an increase in bond strength at the surface of separation of the polar cord/impregnating composition. Experiments showed that the resins increased the bond strength also at the surface of separation of the impregnating layer/rubber (Table VI). The reason for this may be the vulcanizing action of formaldehyde resins, which according to the literature is based on the formation of primary chemical bonds between the resin and rubber molecules[28].

INTRODUCTION OF ALBUMEN

Impregnating compositions with additions of albuminous substances have found great application[1–4]. These substances (casein, albumen, etc.) are added to latex in the form of dispersions, prepared with borax, ammonia, etc.

The introduction of albuminous substances into latex sharply increases the bond strength between cord and rubber (Figure 8). This is explained by the

TABLE VII

EFFECT OF CASEIN ON BOND STRENGTH OF IMPREGNATING LAYER/RUBBER

Characteristics of the system impregnating layer/rubber	Static separation, kg/cm	
	Before heating	After heating
Latex/SKB	0.8	0.36
Latex + 5 parts by weight casein/SKB	1.23	0.44
Latex + 10 parts by weight casein/SKB	2.30	0.55
Latex + 15 parts by weight casein/SKB	2.80	0.70
Latex + 20 parts by weight casein/SKB	3.30	1.40
Latex + 30 parts by weight casein/SKB	4.04	1.20

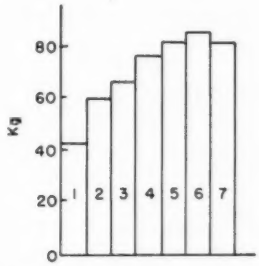


FIG. 8.—Effect of albumen on bond strength between viscose cord and rubber, estimated by the method of pulling down unit threads: *1*. Latex; *2*. Latex +5 parts by weight casein; *3*. Latex +10 parts by weight casein; *4*. Latex +15 parts by weight casein; *5*. Latex +20 parts by weight casein; *6*. Latex +30 parts by weight casein; *7*. Latex +20 parts by weight albumen.

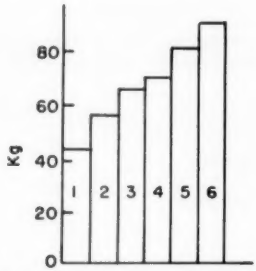


FIG. 9.—Effect of simultaneous introduction of albumens and resins on the bond strength of viscose cord with rubber, estimated by the method of pulling down unit threads: *1*. Latex. *2*. Latex+10 parts by weight phenol formaldehyde resin; *3*. Latex+10 parts by weight casein; *4*. Latex+10 parts by weight phenol formaldehyde resin+10 parts casein; *5*. Latex+20 parts casein; *6*. Latex+20 parts casein+10 parts phenol formaldehyde resin.

presence in the albumen molecule of polar amino groups, interacting with the polar molecules of cellulose.

Our investigations showed that albuminous substances increase the bond strength also at the surface of separation impregnating layer/rubber (Table VII).

INTRODUCTION OF ALBUMEN AND RESINS TOGETHER

The literature contains no information on the simultaneous use of albumens and resins in impregnating compositions.

Our work showed that the simultaneous use of albumens and resins in impregnating compositions leads to a further increase of bond strength (Figure 9). It also intensifies the interaction at the surface of separation impregnating layer/rubber (Table VIII).

USE OF VULCANIZING AGENTS

The desirability of using vulcanizing agents (sulfur and accelerator) in impregnating compositions is a matter of dispute[1]. According to our data, the use of these materials leads to a further increase of bond strength (Figure 10).

In selecting the vulcanizing agents the following questions arose: 1, the necessity for using sulfur, and 2, the necessity for using an activator—zinc oxide. Study of the first question showed that sulfur, migrating from the sur-

TABLE VIII

EFFECT OF SIMULTANEOUS INTRODUCTION OF CASEIN AND RESINS ON BOND STRENGTH OF THE SYSTEM IMPREGNATING LAYER/RUBBER

Characteristics of the system impregnating layer/rubber	Static separation, kg/cm	
	Before heating	After heating
Latex/SKB	0.8	0.36
Latex + 10 parts by weight phenol formaldehyde resin/SKB	1.20	0.53
Latex + 20 parts by weight casein/SKB	3.30	1.40
Latex + 10 parts by weight phenol formaldehyde resin and 20 parts casein/SKB	3.80	1.90

TABLE IX

EFFECT OF SULFUR IN IMPREGNATING COMPOSITIONS ON BOND STABILITY OF IMPREGNATED CORD (7V) WITH RUBBER

Sulfur, parts by weight	Accelerator group MBTS+DPG		Accelerator dimethylamine salt of MBT (DMASK)	
	Pull down, kg	Repeated compression, min	Pull down, kg	Repeated compression, min
Without sulfur	96.0	120	95.0	140
0.5	98.0	60	—	—
1.0	99.0	51	—	—
1.5	97.0	48	—	—
2.0	96.0	40	96.0	80

face layer of the rubber, is sufficient to vulcanize the thin film of adhesive (Table IX). This is confirmed by chemical analysis which shows that the amount of sulfur migrating is as much as 2%.

From the data obtained it is clear that the use of sulfur in impregnating compositions is not recommended. The drop in bond strength under dynamic deformation shows that the use of sulfur in impregnating compositions leads to over-vulcanization of the adjoining layer.

Examination of the second question shows that the use of zinc oxide depends on the accelerator employed (Table X). Some accelerators, e.g., the water soluble dimethylamine salt of MBT, do not call for the inclusion of zinc oxide in the impregnating material.

Our investigations showed:

1. Pure latex, without polar substances, does not increase the cord/rubber bond strength.

2. An increase of bond strength of cord/rubber compositions based on latex is obtained by the introduction into the latex of polar substances (albumen, resins) containing the groups NH_2, OH, etc.

3. The use of accelerators leads to a marked increase in cord/rubber bond strength.

4. The use of sulfur in impregnating compositions is unsuitable, as sulfur migrating from the surface layers is sufficient to vulcanize the adhesive film.

5. The use of zinc oxide in impregnating compositions depends on the accelerator groups present.

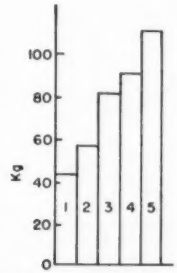


FIG. 10.—Effect of vulcanizing groups on bond strength of a viscose cord with rubber (pull down of unit threads); *1.* Latex; *2.* Latex+10 parts by weight phenol formaldehyde resin; *3.* Latex+20 parts casein; *4.* Latex+20 parts casein+10 parts phenol formaldehyde resin; *5.* Latex+20 parts casein+10 parts phenol formaldehyde resin+accelerator groups.

TABLE X

EFFECT OF THE ZINC OXIDE IN IMPREGNATING COMPOSITIONS ON BOND STABILITY OF IMPREGNATED CORD (7V) WITH RUBBER

Zinc oxide, parts by weight	Accelerator group MBTS+DPG		Accelerator dimethylamine salt of MBT (DMASK)	
	Pull down, kg	Repeated compression, min	Pull down, kg	Repeated compression, min
Without zinc oxide	90.0	98	95.0	140
1.0	92.0	110	94.0	120
3.0	94.0	112	94.0	150
5.0	96.0	120	93.0	145

THE EFFECT OF PHYSICO-MECHANICAL PROPERTIES OF THE ADHESIVE FILM

The literature contains considerable data on the effect of physico mechanical properties of the adhesive film in increasing bond strength. The basic work in this field concerns the system undersurface/adhesive. Concerning the system cord/impregnating layer/rubber there are a number of separate ideas, not backed up by the experimental data. Thus Gillman and Thoman[2] consider that the film of impregnating layer should be heat-stable and flexible so that there shall be no transmission of brittleness to the impregnated cord. Springer[1] on the other hand considers that it is necessary to make the film stiffer, increasing its casein content up to 50%. Other investigators also recommend increasing the stiffness of the impregnating layer, introducing zinc oxide[4]. There is some information about the relationship of cord/rubber bond strength to increased modulus and elastic properties of films of impregnating materials[20–22].

In our investigations we paid considerable attention to the effect of the physico mechanical properties on the bond strength[14]. It was found that the introduction of substances changing the chemical composition of the adhesive

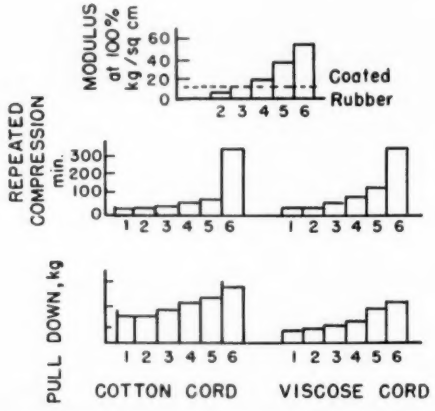


FIG. 11.—Bond strength of impregnated cord/rubber and modulus of adhesive film in relation to impregnating composition. *1*. Impregnated cord; *2*. Latex; *3*. Latex+phenol-formaldehyde resin; *4*. Latex +casein; *5*. Latex+resin+casein; *6*. Latex+resin+casein+accelerator.

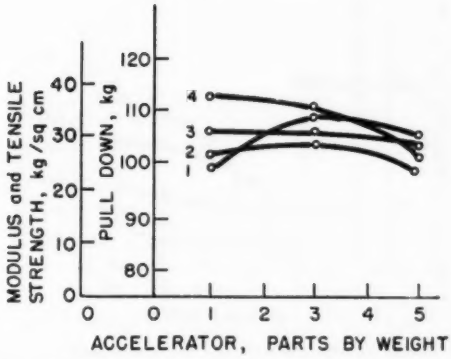


FIG. 12.—Effect of accelerator 226 on bond strength and physicom echanical properties of layer; *1*. Pull down, kg; *2*. Modulus @ 50%, kg/cm²; *3*. Modulus @ 100%, kg/cm²; *4*. Tensile strength, kg/cm².

film lead at the same time to a change in the physico mechanical properties of the film and to increased modulus (Figure 11).

The physico mechanical properties of a film of impregnating material can be changed by changing the accelerator groups, the amount of casein or by introducing active fillers etc.

Let us examine the effect of each physico mechanical characteristic of a film of impregnating material on the strength of the cord/rubber bond.

TENSILE STRENGTH OF FILMS

Our investigation showed that no relationship can be found between the tensile strength of the films of impregnating layer and the bond strength. This is clear from the following data:

Effect of accelerator.—The introduction of an increasing quantity of water-soluble accelerator 226 (triethanolamine salt of MBT), leads to an increase in

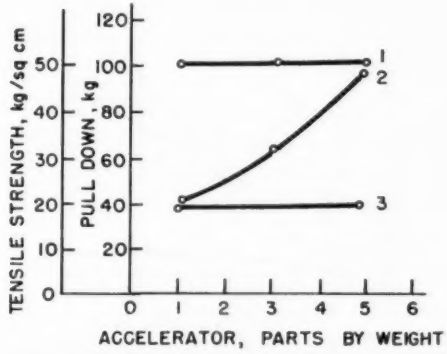


FIG. 13.—Effect of accelerator 228 on bond strength and physico mechanical properties. *1*. Pull down, kg; *2*. Tensile strength, kg/cm²; *3*. Modulus at 50%, kg/cm².

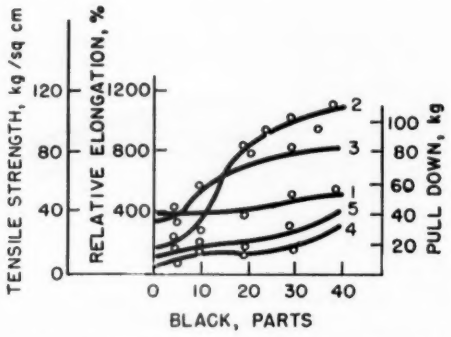


FIG. 14.—Effect of black on the properties of the films and bond strength: *1*. Pull down, kg; *2*. Tensile strength, kg/cm²; *3*. Relative elongation, %; *4*. Modulus at 80%, kg/cm²; *5*. Modulus at 100%, kg/cm².

the bond stability, producing simultaneously a fall in tensile strength of the films (Figure 12). The introduction of the water-soluble Accelerator 228 (monoethanolamine salt of MBT) causes an increase in tensile strength but no increase in cord/rubber bond strength (Figure 13).

Effect of finely dispersed gas black.—The use of finely divided gas black leads to a significant increase in tensile strength but does not noticeably alter the cord/rubber bond strength (Figure 14).

Effect of use of black and casein together.—In the case of the simultaneous use in latex of casein and black, we get a fall in tensile strength and a sharp increase in cord/rubber bond strength.

MODULUS OF FILMS

The curve of deformation/stress of an impregnating layer is of an unusual character and differs from the curve deformation/stress for the rubber layer itself (Figure 15).

The special peculiarity of a film of impregnating material is its capacity to give an increased value for the modulus (above 20 kg/cm²), in the region of

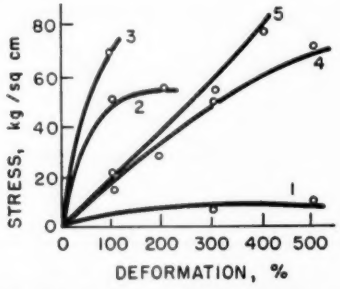


FIG. 15.—Stress/deformation curve for impregnating film and rubber layer: *1*. Latex; *2*. Impregnating composition 50-u; *3*. Impregnating composition 30-DS; *4*. Rubber layer 100% synthetic rubber; *5*. Rubber layer 100% natural rubber.

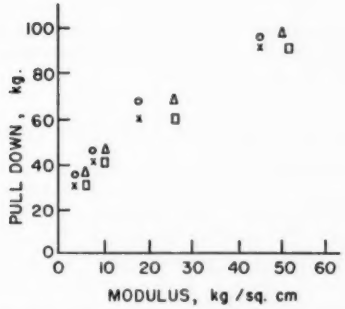


FIG. 16.—Relation of bond strength to modulus of impregnating film.

small deformations (50–100%). Further deformation does not give any increase in film modulus, while in case of an ordinary rubber mix the modulus increases uniformly in proportion to the increase in deformation.

The rubber and textile layers in tires do not undergo very great deformations (less than 100%), and it is therefore interesting to study the behavior of the adhesive layers in such a region of small deformation. The rubber layers under small deformations (up to 100%) show quite small moduli (up to 20 kg/cm^2).

From the data in Figure 15 it is evident that the films of impregnating material have a modulus significantly greater than the rubber mix itself.

Our experimental data showed there is a straight line relationship between the value of the modulus in the region of small deformation and the bond strength (Figure 16).

Effect of accelerator.—An accelerator introduced into the impregnating material increases the bond strength if it increases the modulus of the impregnating layer (Figures 12 and 13).

Effect of casein.—Casein, introduced into the latex, increases the modulus of the impregnating layer and the bond strength cord/rubber (Figure 17).

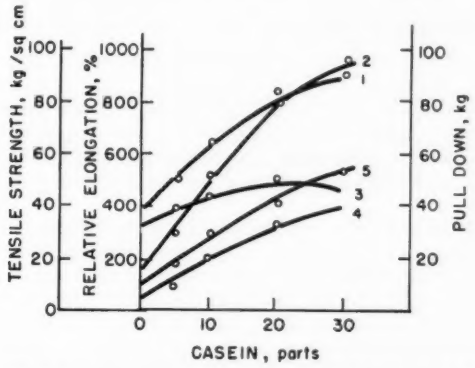


FIG. 17.—Effect of casein on properties of film and bond strength. *1.* Pull down, kg; *3.* Elongation, %; *4.* Modulus at 50%, kg/cm^2; *5.* Modulus at 100%, kg/cm^2.

Effect of black and casein.—Black in latex does not increase the modulus of the impregnating film and the bond strength (Figure 14). The simultaneous use of black and casein produces an increase in modulus of the impregnating layer and the cord/rubber bond strength.

RELATIVE ELONGATION OF FILM

The effect of the elongation of films of impregnating material on the cord/rubber bond strength has been studied in mixes with different accelerator groups in the impregnating material and the introduction of fillers (black, resins, etc.).

Effect of accelerator.—The work of Dogadkin, Reznikovski and Fel'dshtein showed that the bond strength of pliedup systems is increased due to a retardation of the process of vulcanization in the first stage. This retardation is produced through the vulcanizing systems, an induction period of vulcanization being assumed.

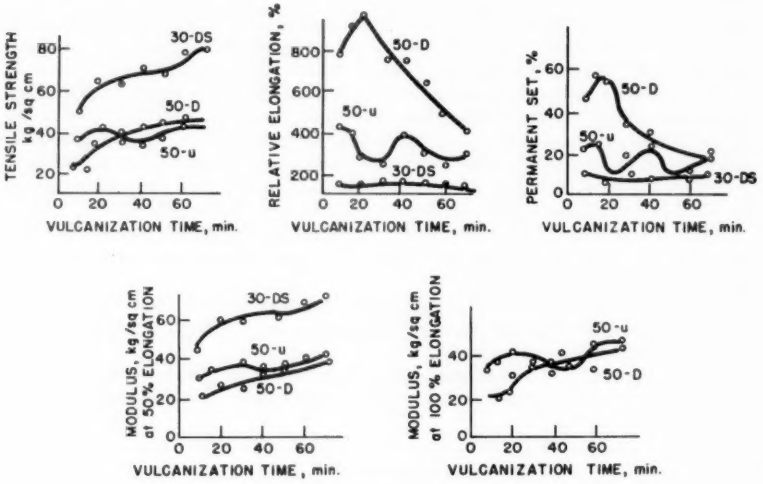


FIG. 18.—Physico mechanical properties of impregnating films.

To explain the effect of the induction period of vulcanization in the system cord/impregnating layer/rubber we studied two impregnating materials, differing in their accelerator groups. In the first we used MBTS + DPG in the presence of zinc oxide, and in the second the water-soluble dimethylamine salt of MBT.

The data for the kinetics of vulcanization, shown in Figure 18, indicate that, using dimethylamine salt of MBT it is possible to observe the retardation effect in the first vulcanization stage. In this case we obtain a film with much higher relative elongation and permanent set, at the same time maintaining the remaining physico mechanical properties at the same level as those of the film with the first accelerator groups.

An increase in the relative elongation of the film and the appearance of retardation during the first period of vulcanization with the dimethylamine

TABLE XI

BOND STRENGTH OF VISCOSE CORD 13V, IMPREGNATED WITH 50-u AND 50-D BASED ON SKB RUBBER

Impregnating composition	Pulldown, kg	Repeated compression, min	Repeated flexing, cycles
50-u	95.0	207	390
50-D	95.0	215	365

salt of MBT did not lead to an increase in bond strength between impregnated cord and rubber (Table XI) but an increase in bond strength of the pliedup system impregnating layer/rubber was observed (Table XII).

The difference in the effects of flow and elongation of an adhesive film in a pliedup system and in the system cord/impregnating layer/rubber can be explained by the fact that in the system rubber/adhesive it is important that the adhesive shall fill all the irregularities in the rubber surface. For this to happen it is essential that the adhesive shall be in a viscous condition for an appreciable period of time. In the case of the system cord/impregnating layer/rubber the flow of the impregnating material takes place during the soaking

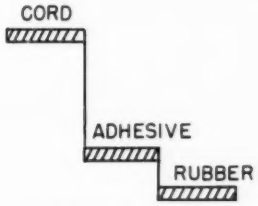


FIG. 19.—Diagram of distribution of components in the system cord/adhesive/rubber, by modulus.

process. Thus, during vulcanization the most important role is played by the viscosity of the casing rubber.

Effect of carbon black and resin.—The use of carbon black in a composition leads to a reduction in the relative elongation of the impregnating layer, to the disappearance of the period of viscosity in the first vulcanization stage, and produces a sharp increase in bond strength.

The removal of phenol formaldehyde resin from a black-latex dispersion causes an increase in relative elongation, a decrease in modulus of the film and a fall in bond strength. From these facts we can draw some conclusions about the positive effect of a reduction in elongation of the film of impregnating material on the adhesion.

TABLE XII

BOND STABILITY OF SYSTEM IMPREGNATING LAYER/RUBBER IN RELATION TO ACCELERATOR

System (cord/rubber)	Static separation, kg/cm		Dynamic separation, cycles	
	Before heating	After heating	Flexing	Compression
50-u—SKB	2.3	2.15	257	255
50-D—SKB	3.3	2.30	485	348.5

The work we have done demonstrates the important role played by the physico mechanical properties of a film of impregnating material—especially the relative elongation and modulus at small elongations.

In a running tire stresses arise at the surface of separation of cord/rubber, which, due to the difference in the physico mechanical properties of these materials, can lead to separation.

A film of impregnating material whose modulus at small elongations exceeds the modulus of the rubber itself, and whose relative elongation is much less than that of the rubber, can play the part of an intermediate "bridge", taking itself part of the stresses in the working system (Figure 19).

The work carried out showed that:

1. The stability of a film of impregnating material does not have a direct influence on the bond strength of impregnated cord/rubber.
2. Modulus of a film of impregnating material in the range of small deformations shows a straight line relationship with the bond strength; the higher the modulus of the film, the higher the bond strength with rubber.
3. A much lower value of the relative elongation of the impregnating material leads to an increase in bond strength of the system.
4. A film of impregnating material may act as an intermediate bridge between materials (cord and rubber) differing in physico mechanical characteristics.

PRINCIPLES OF FORMULATING IMPREGNATING COMPOSITIONS BASED ON LATEX DISPERSIONS

Study of the experimental material shows that the bond strength in the system cord/impregnating layer/rubber is determined by a series of factors. The basic factors which we took into account in formulating impregnating compositions are:

The intermolecular and chemical interaction at the surfaces of separation cord/impregnating material and impregnating material/rubber;

The physico mechanical properties of a film of impregnating material (modulus and relative elongation).

From what has been said it follows that in making formulations of this kind the following points must be borne in mind:

1. Latexes used as a basis for impregnating compositions must possess stability to repeated breakdown, to mechanical and temperature action and to the effect of added ingredients.
2. The amount of material deposited on the cord should fall within the limits 8–12%.
3. The impregnating material should promote increased surface of the impregnated cord.
4. To increase the cord/rubber bond strength it is necessary to introduce into the latex polar substances (albumen, resin), containing NH_2, OH groups etc. and also accelerators of vulcanization.
5. To ensure uniformity of the impregnating composition and to improve the technical properties, the use of water soluble accelerators is recommended (dimethylamine salt of MBT, etc.).
6. It is essential to introduce into the impregnating material substances which ensure specific physico mechanical properties of the film (high modulur

at small elongations—up to 100%—exceeding the modulus of the rubber layes itself, and a low relative elongation).

With the above considerations in mind we worked out first of all production impregnating composition 50-u which, in spite of the increased cord/rubber bond strength (2–3 times that in the case of unimpregnated cord), possesses certain deficiencies:

Insufficient stability of the dispersion due to the use of free-flowing ingredients (MBTS, DPG, zinc oxide);

The smooth surface of the impregnated cord (Figure 5);

Adhesion-type separation at the surface between impregnating layer and rubber.

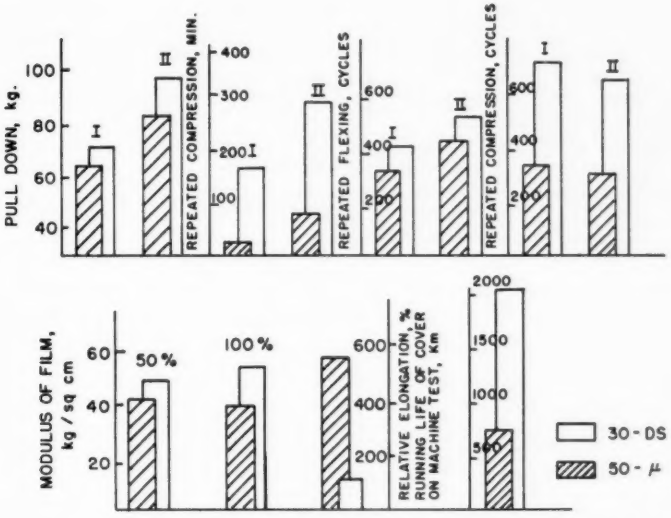


FIG. 20.—Comparative characteristics of impregnating compositions 50-u and 30-DS. I. Background rubber based on 100% SKB for first carcass layer. II. Background rubber based on 100% SKB for subsequent carcass layers.

A further increase of bond strength with latex impregnating compositions is obtained with the use of water soluble accelerators and finely dispersed blacks. Thus the introduction into a latex-casein-phenol formaldehyde dispersion of 30 parts finely dispersed channel black and the water soluble accelerator dimethylamine salt of MBT leads to a noticeable increase of bond strength of the impregnated cord/rubber by comparison with the material 50-u.

The use of a black dispersion increases the modulus of the film (Figure 20) and produces a loosened surface of the impregnated viscose cord (Figure 6). This in its turn increases the cord/rubber bond strength and the running life of a cover on machine test. At the same time the use of the improved impregnating material 30-DS changes the character of separation: breakdown occurs in the rubber (cohesion type) or in the cord and rubber (combined type).

Thus using the improved composition 30-DS we eliminate the deficiencies of 50-u the stability of the dispersion is increased due to the use of a water soluble accelerator; surface loosening is produced; the character of separation is changed.

REFERENCES

[1] Springer, A., *Kautschuk u. Gummi* **3**, 355, 398, 439 (1950); RABRM Transl. 312.
[2] Gillman, H. and Thoman, R., *Ind. Eng. Chem.* **40**, 1237 (1948).
[3] Litzler, C., *Rubber Age* (N. Y.) **71**, 501, 630, 781 (1950).
[4] Bramley, A., *Rubber Age and Synthetics* **33** (1952).
[5] Suziki, Takeo, Aokia, Junji and Urabe, Nobuaki, *J. Soc. Rubber Ind.* **26**, 6 (1953).
[6] Illingworth, J., *Rubber Age* (N. Y.) **73**, 657 (1953).
[7] Gardner, E. and Williams, P., *Proc. Second Rubber Technol. Conf.*, London, **1948**, p. 478.
[8] Deryagin, B. V. and Krotova, N. A., "Adhesion" Izd. AN SSSR., 1949.
[9] Yabko, Ya. M. and Voyutskif, S. S., *Tekst. Prom.* **1951**, No. 7.
[10] Yabko, Ya. M. and Voyutskif, S. S., *Tekst. Prom.* **1952**, No. 7, 39–40; in German, *Plaste u. Kautschuk* **1**, 136 (1954).
[11] Voyutskif, S. S. and Yabko, Ya. M., *Tekst. Prom.*, **1950**, No. 2, 26.
[12] Yabko, Ya. M. and Voyutskif, S. S., *Tekst. Prom.* **1953**, No. 1, 33.
[13] Hauser, E., *Rubber Age* (N. Y.) **32**, 342 (1933).
[14] Uzina, R. V., Symposium, "Production and Use of Synthetic Latexes", Goskhimizdat, 1953, p. 61.
[15] Murphy, R., Baker, L. and Reinhardt, R., *Ind. Eng. Chem.* **40**, 2292 (1948).
[16] Wake, W. C. (reference not identified).
[17] Borroff, E., Khot, R. and Wake, W. C., *Ind. Eng. Chem.* **43**, 439 (1951).
[18] Suziki, Takeo, Aokia, Junji and Urabe, Nobuaki, *J. Soc. Rubber Ind.* **26**, 8 (1953).
[19] Hammond, G. and Moakes, R. C. W., RUBBER CHEM. & TECHNOL. **23**, 467 (1950).
[20] *Rubber Age* (N. Y.) **65**, 161 (1949).
[21] Voyutskif, S. S., Rebinder, P. A. et al., *DAN SSSR* **73**, 747 (1950).
[22] Moakes, R. C. W., *Ind. Rubber J.* **121**, 719 (1951).
[23] Meyrick, T. and Watts, J., *Trans. Inst. Rubber Ind.* **25**, 159 (1949).
[24] *India Rubber World* **127**, 578 (1953).
[25] Meyrick, T. and Watts, J., *India Rubber J.* **122**, 467 (1952).
[26] Profft, E., *Chem. Z.* **75**, 223 (1951); abridged, in French, *Rev. gen. Caout.* **29**, 409, 71 (1952).
[27] Deryagin, B. V., *Vestnik AN SSSR*, No. 7, 10 (1954).
[28] Meer, L., RUBBER CHEM. & TECHNOL. **18**, 853 (1945).

BOND STRENGTH OF TREAD AND BREAKER STOCKS UNDER REPEATED DEFORMATIONS *

I. A. Levitin, Yu. G. Korablev, A. E. Kornev, and B. L. Babitskiĭ

As the tire industry changed over to production from synthetic rubber a new form of service failure was encountered—stripping of the tread from the breaker. This phenomenon is most noticeable where SBR rubbers are used, and also at the boundary layer of pliedup rubbers differing in composition, having different moduli and different degree of cure in the zone of contact with each other.

In recent times there have been carried out a considerable number of investigations of the dynamic strength of a system of pliedup rubbers. The results show that an important influence is exerted upon the bond strength of pliedup rubbers by their flow, which governs the increase in contact area in the boundary layers, by the diffusion of the separate links of the chain molecules of one pliedup layer into the other by the degree of the pliedup rubbers, and the bonding layers between the layers of rubber. The compounding ingredients also affect the bond strength.

As a result a number of technological measures were taken to increase bond strength between the components of tires on the adoption of SBR in the industry. These were directed towards increasing the surface contact between the layers, and towards improving the surface of the semifinished products before plyingup.

An important effect upon the improvement of the surface properties of tires was evidenced by increased pressure in the building process, roughening of the tread and breaker, pressing of the uncured casings after building, and introducing into tire formulas accelerator groups which ensure increase in the time spent by the stocks in the viscous flow state in the initial period of vulcanization.

One method of attaining higher dynamic strength in the tread-breaker system was some increase in the modulus of the breaker rubber by increaisng the amount of channel black. A recently developed formula for tread rubber with increased elasticity and for a stiff breaker noticeably reduced the failures of tires from stripping of the tread from the breaker. Nevertheless this problem still occupies the center of attention in the industry.

EXPERIMENTAL

For the test we selected a machine for repeated compression with constant static loading. This machine was of the type MMS-1, making it possible to test standard specimens under conditions approximating to those of the behavior of the tread portion of tires in service. A feature of this machine in comparison with other apparatuses for repeated compression testing of rubber is that during the test the specimen, while undergoing alternating compress at a high rate, is

* Prochnost' Svyazi Protektornykh I Brekernykh Rezin pri Mnogokratnykh Deformatsiyakh. Translated by R. J. Moseley from *Prochnost' Svyazi . . .*', 1954, pages 173–183.

also under a constant initial load. The machine makes it possible to vary the magnitude of the initial load upon the specimen, the amplitude and frequency of deformation of the specimen, and also to carry out tests at room temperature and above.

The specimens for testing consist of cylinders with a diagonally arranged layer of breaker rubber between two layers of tread rubber.

To prepare the specimens, sheets of tread rubber of thickness 9 mm and of breaker rubber of thickness 2 mm were produced on a laboratory mill. After standing for 2 h, slabs of total thickness 38 mm were pliedup from the sheet rubber: two layers each of 9 mm of tread rubber, a layer of breaker rubber and on top of this two further layers of tread rubber (Figure 1a).

The rolling was by a hand roller of weight 1 kg.

Vulcanization of the pliedup sheets was carried out in molds at 143° in a hydraulic press. After vulcanization the slab was left to stand for 24 h, and then was cut up into strips of width 26 to 28 mm (Figure 1, top right). The rectangular bars thus produced were marked up from the end with sloping lines

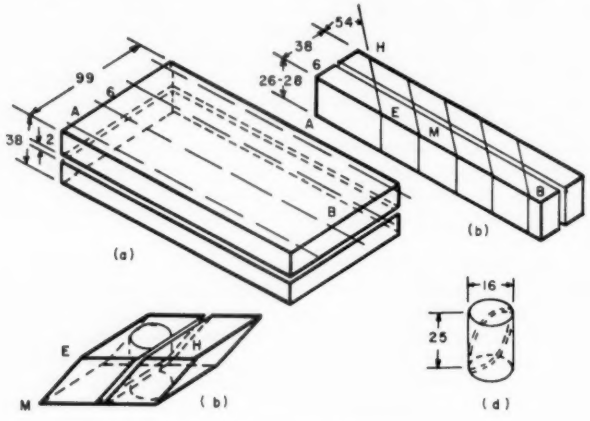


FIG. 1.—Preparation of specimen.

at an angle of 54° with a special template and were cut up into parallelepipeds (Figure 1, lower left), from which we proceeded to cut with a circular knife cylinders of diameter 16 mm (Figure 1, lower right). The ends of the specimens were ground down on an emery wheel to a height of 25 mm.

In choosing the pattern of testing it was observed that not only the length of service life of the specimens, but also the nature of the failure, depend upon the experimental conditions.

The stability of a system of pliedup stocks under conditions of repeated deformations is determined on the one hand by the bond strength between them, and on the other hand by the dynamic strength of the rubbers themselves working in interaction.

The dynamic stability and the nature of the failure are affected by the ratio of the moduli of the tread and breaker rubbers, and also by the conditions of testing of the specimens.

In the case of a high frequency of deformation and relatively low initial compression loading we naturally observe separation at the point of contact between tread and breaker. On the other hand, with high loadings and relatively low frequency of deformation we get failure of the tread and breaker close to the surface of separation.

In line with the problems being investigated we selected conditions of conduct of the dynamic tests such that the pliedup specimens failed predominantly as a result of stripping of the tread from the breaker.

In all cases the frequency of deformation was 850 c/min, the static loading on the specimen 10 kg, the amplitude of deformation for SKS-30 tread rubber 30%; while for more elastic rubbers based on SKS-30A, so as to shorten the time of testing it was 36%.

The method used for assessment of the dynamic stability of pliedup rubbers gives good reproducibility of results and may be used also for investigation of rubber fabric specimens cut directly out of tires.

As a result of these experiments we obtained the following data on the stability of tread rubbers in combination with the breaker.

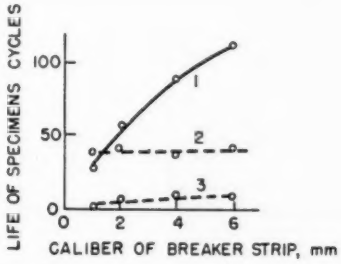


FIG. 2.—Dynamic strength of plied up rubbers with different thickness of breaker layer. *1*—breaker of natural rubber with carbon black. *2*—breaker of SKB. *3*—breaker of natural rubber without carbon black.

Influence of the composition and thickness of the breaker rubber.—We investigated pliedup vulcanizates with a tread based on SKS-30 and breaker of natural rubber with and without carbon black, and also with a breaker of sodium-butadiene rubber. The thickness ("caliber") of the breaker rubber varied from 1 to 6 mm. The results of the tests of the specimens, presented in Figure 2, indicate that for dynamic stability of pliedup specimens up to break the breaker rubbers come in the following order: Natural rubber with carbon black > SKB > natural rubber without carbon black.

Increasing the thickness of a breaker strip of natural rubber with carbon black greatly increases the stripping resistance of the pliedup vulcanizates.

In a breaker strip of sodium-butadiene rubber we did not observe stripping under the experimental conditions, but the specimens failed as a result of fatigue in the breaker rubber itself, at approximately the same time for all the thicknesses.

The influence of the thickness of the breaker strip of natural rubber with carbon black upon bond strength was followed also on standard specimens with cord. Instead of one tread (sic—Transl.) layer, the vulcanizates with cord had layers of rubberized 94T cord pliedup crosswise, of total thickness 18 mm.

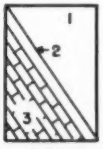
TABLE I

DYNAMIC STRENGTH OF PLIEDUP VULCANIZATES OF NATURAL RUBBER WITH CORD WITH VARYING THICKNESS OF BREAKER LAYER

Thickness of breaker layer, mm	Life up to ply separation, cycles
1	2550
2	4250
3	13600

From the data in Table I it may be seen that the life of the specimens with cord likewise increases sharply as the thickness of the breaker rubber. Separation in the present case was observed predominantly between the casing rubber and the cord, which fact should be attributed to the considerable shear forces at the boundary of the elastic rubber and the stiff cord when the bond strength between them is inadequate.

We note that the resulting data on the enhancement of the dynamic strength of standard pliedup specimens on increasing the thickness of the breaker strip agree well with practical experience. The previous increase in the rubber content of the natural rubber breaker noticeably improved the service properties of 9.00–20 size tires.



Construction of Plied up Specimen with Cord

1. Tread face
2. Breaker layer
3. Layer of plied up rubberized cord

FIG. 3.—Construction of pliedup specimen with cord. *1*—tread face. *2*—breaker layer. *3*—layer of pliedup rubberized cord.

Treatment of the surface before plying-up.—In Table II we give data on the influence of treating the semifinished tread and breaker rubbers with naphtha and a cement based on natural rubber with carbon black upon the bond strength of the vulcanizates.

The use of naphtha or of a carbon black/natural rubber cement for treatment of pliedup semifinished products of SKS-30 tread rubber and breaker of natural rubber with carbon black somewhat increases the resistance of the vulcanizates to dynamic separation.

Influence of the duration of thermoplasticization of SKS-30A.—In the present series of tests we studied the dynamic strength of pliedup vulcanized rubbers with breaker of SKB and tread of SKS-30A, plasticized in an autoclave at 135° over different periods.

In Figure 4 we collate the plasticity of the original SKS-30A, the mechanical properties of a vulcanizate of tread rubber and the dynamic strength of the pliedup specimens.

The resulting data indicate the sharp reduction in the fatigue strength of the pliedup rubbers as the duration of thermoplastication of the rubber used for making the tread is increased. The most rapid fall-off in the fatigue strength

TABLE II

INFLUENCE OF TREATMENT OF PLIEDUP SURFACES UPON THE SEPARATION RESISTANCE OF VULCANIZED RUBBERS (SKS-30A TREAD RUBBER, BREAKER OF NATURAL RUBBER WITH CARBON BLACK)

Type of treatment of surface	Life before separation, cycles
Untreated surface	44,200
Freshening-up with naphtha	59,500
Cement, concentration 4.5%	64,600
Cement, concentration 8%	74,700

of the vulcanizates is observed at the commencement of thermoplastication, when the Defo hardness of the SKS-30A falls most sharply.

The impairment of the fatigue properties of the tread breaker system is possibly connected with the oxidative processes in the SKS-30A rubber itself during thermoplastication, as well as with the considerable reduction in the modulus and the increase in the relative elongation of the tread layer.

It must be pointed out that stripping of the softer thermoplasticate occurs mainly as a result of failure of the tread layer at the boundary with the breaker.

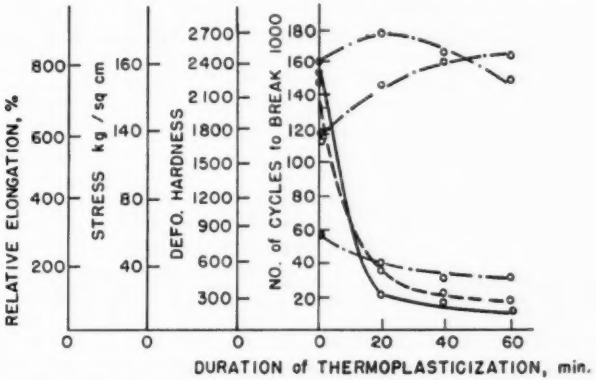


FIG. 4.—Plasticity of a thermoplasticate, mechanical properties of tread rubbers and resistance to separation of specimens pliedup with SKB breaker, as a function of the time of thermoplasticization of the SKS-30A. *1*—relative elongation. *2*—tensile strength. *3*—300% modulus. *4*—Defo hardness of SKS-30A thermoplasticate. *5*—life of specimens pliedup with breaker.

This type of failure is connected with the stress concentration in the tread rubber, with the relatively high elongation and low modulus in interaction with the stiff and little-stressed breaker of sodium-butadiene rubber.

Duration of vulcanization and stripping resistance of pliedup rubbers.—It is well known that the optimum cure of rubber for tensile strength does not coincide with the optimum for fatigue properties. It was therefore of interest to test the influence of the time of vulcanization upon the stability of pliedup rubbers working under conditions of repeated compression.

In Figure 5 we show the influence of time of vulcanization (at 143°) upon the dynamic bond strength of SKS-30 based tread rubbers and breakers of natural rubber with carbon black and of sodium-butadiene rubber.

As may be seen from the figure, the separation resistance of the rubbers increases greatly as the time of vulcanization is increased.

In Table III we give the mechanical test data for tread and breaker rubbers. The dumbbell specimens for these tests were blanked out from the same sheets as were used for preparing the cylinder specimens for repeated compression.

The data in Table III and Figure 5 allow us to conclude that the time to reach optimum cure for tensile strength is much less than that for reaching optimum cure for resistance of the rubbers to dynamic stripping.

The increase in the fatigue strength of the pliedup specimens in a given routine of testing is apparently connected with possible structural changes in the boundary layer in the process of further vulcanization, and also with the reduction of elongation and increase in stiffness.

The increase observed in the dynamic bond strength on increasing the duration of vulcanization has to be taken into account in planning practical routines for vulcanization of multiple rubber articles to operate under conditions of repeated deformations.

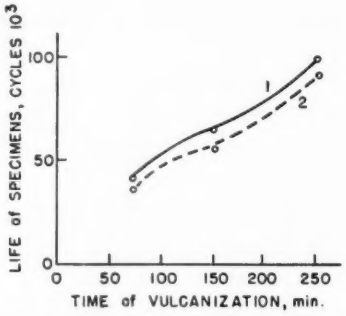


FIG. 5.—Influence of duration of vulcanization upon the dynamic strength of pliedup tread (SKS-30A) and breaker (natural or SKB) rubbers. *1*—breaker of natural rubber with carbon black. *2*—breaker of SKB (thickness 2 mm).

Influence of the vulcanization groups in tread rubber.—The amount of sulfur and accelerators in the tread layer has an important influence upon the service properties of a pliedup rubber system.

In Tables IV and V we collate the mechanical properties of SKS-30A tread

TABLE III

MECHANICAL PROPERTIES OF TREAD AND BREAKER RUBBER

	Time of cure of slabs, min	200% modulus, kg/sq cm	Tensile strength, kg/sq cm	Relative elongation, %	Permanent set, %	Shore hardness
	70	35	130	678	15	64
Tread	100	36	144	560	15	63
SKS-30	150	35	132	578	15	64
	250	35	126	525	12	62
	70	31	56	340	7	55
Breaker	100	37	76	380	6	53
SKB	150	40	65	325	4	56
	250	—	60	305	3	52

TABLE IV

MECHANICAL PROPERTIES OF SKS–30A TREAD RUBBERS WITH DIFFERENT AMOUNTS OF SULFUR

Amount of sulfur, phr	1.7	1.9	2.0	2.5	3.0
Bound sulfur	1.67	1.87	1.97	2.46	2.78
Tensile strength, kg/sq cm	181	182	170	172	178
300% modulus, kg/sq cm	34	51	54	70	70
Relative elongation, %	790	730	692	622	607
Tear resistance, kg/cm	66	65	64	58	53
Rebound elasticity, %	46	47	46	44	45
Shore hardness	58	60	61	63	64
Crack growth resistance, thousands of cycles	120.0	87.4	73.8	41.6	31.2
Life of pliedup tread breaker system in repeated compression, thousands of cycles	17.8	19.6	16.4	97.0	158.0
Temperature of failure of pliedup specimens, ° C	163	161	161	155	137

rubbers, containing different amounts of sulfur and different accelerator groups, with the dynamic endurance of pliedup specimens (breaker strip of sodium-butadiene rubber).

It is seen from the data that on increasing the content of sulfur in the tread rubber there is a sharp increase in the fatigue resistance of the pliedup tread breaker system under repeated compression and at the same time there is a noticeable reduction in the temperature inside the specimens at the instant of failure. At the same time there is a reduction in the relative elongation and increase in the stiffness (modulus) of tread rubber. The tensile strength does not alter significantly.

Thus, raising the degree of vulcanization of SKS-30A tread rubber, which effects a reduction in the relative elongation with simultaneous increase of the stiffness, has an advantageous effect upon its bond strength with the breaker under the above conditions of testing.

The superiority of the accelerator BT sulfenamide over the MBTS-DPG accelerator group in SKS-30A tread rubber is evident in the dynamic properties of the tread breaker system only with the amount of 2 parts by weight of sulfur (Table V).

We may assume that, along with the reduction in relative elongation and increasing the modulus, a lowering of the temperature during repeated com-

TABLE V

BOND STRENGTH AND MECHANICAL PROPERTIES OF SKS–30A TREAD RUBBERS WITH DIFFERENT VULCANIZATION GROUPS

Accelerator group, parts by weight				Sulfur, parts by weight	300% modulus, kg/sq cm	Tensile strength, kg/sq cm	Relative elongation, %	Bond strength of tread with breaker, ths. of cycles
Sulfenamide BT	MBTS	DPG	Thiuram					
1.4	0.2	—	—	2	58	187	710	26.3
1.2	0.3	—	—	2	64	199	687	27.2
1.4	—	—	0.1	2	60	185	687	25.5
—	1.0	1.0	—	2	45	175	772	15.3
1.4	0.2	—	—	1.7	48	181	790	17.8
1.2	0.3	—	—	1.7	42	178	825	12.8
1.4	—	—	0.1	1.7	51	186	750	17.8

pression plays a significant role in enhancing the dynamic strength of pliedup rubbers.

Vulcanizates with increased content of bound sulfur have a greater concentration of transverse chemical bonds between the chain molecules of the rubber. This is responsible for a reduction in heat buildup and a weakening of relaxation phenomena during cyclic deformations, and also an increase in the fatigue strength of the tread rubber and in the bond strength at the tread breaker boundary. It must be taken into account however that increasing the amounts of sulfur is accompanied by a considerable reduction in the resistance of the tread rubbers to crack growth in repeated flexing (Table IV).

Thus the amount of sulfur must be decided with regard to both these factors. The raising of the intensity of structure formation as a result of vulcanization, and the related increase in stiffness, the reduction in elongation and the increase in the dynamic stability of pliedup rubbers may be achieved not only on account of the sulfur, but also on account of the amounts of accelerators.

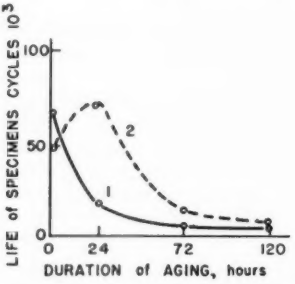


FIG. 6.—Influence of thermal aging upon the separation resistance of pliedup rubbers. *1*—breaker of natural rubber with carbon black. *2*—breaker of SKB (thickness 2 mm).

In Table VI we present bond strength figures for pliedup rubbers with different amounts of BT sulfenamide and of MBTS in a SKS-30A tread.

These data indicate the increase in fatigue strength of the tread breaker system with increased content of the accelerators BT sulfenamide and MBTS in tread rubber.

Influence of thermal aging upon separation resistance of vulcanized rubbers.—Cylindrical pliedup specimens with SKS-30 tread were subjected to thermal

TABLE VI

DYNAMIC BOND STRENGTH OF PLIEDUP SKS-30A RUBBERS WITH DIFFERENT AMOUNTS OF MBTS AND BT SULFENAMIDE IN THE TREAD
(Amount of sulfur in the mix, 2 phr)

Sulfenamide BT, phr	MBTS, phr	Bound sulfur, %	300% modulus, kg/sq cm	Tensile strength, kg/sq cm	Relative elongation, %	Bond strength, ths. cycles
0.8	0.2	1,896	26	150	882	10.2
1.0	0.2	1,937	34	152	795	14.5
1.2	0.2	1,957	38	171	752	19.6
1.4	0.2	1,966	54	170	692	26.4
1.2	0.0	1,953	39	156	765	13.6
1.2	0.3	1,970	58	164	685	21.2
1.2	0.4	1,976	59	161	650	27.2

TABLE VII

LIFE OF PLIEDUP RUBBERS UP TO FAILURE, WITH VARIOUS ANTIOXIDANTS IN THE BREAKER (TREAD OF SKS–30, BREAKER OF SKB)

	Life of pliedup specimens, ths. cycles	Life of pliedup specimens after 120 h thermal aging, ths. cycles
Phenyl-2-naphthylamine, 1.5 phr	51.0	4250
Phenyl-2-naphthylamine, 1.5 phr; 4,4'-diphenylphenylene diamine, 0.2 phr	59.5	5100
Phenyl-2-naphthylamine, 1.5 phr; *p*-anisidine, 0.2 phr	81.6	12900
Phenyl-2-naphthylamine, 1.5 phr; 4,4'-diphenylphenylene diamine, 0.2 phr; *p*-anisidine, 0.2 phr	66.3	7650

aging in an air thermostat at 100°, and were then tested by the standard method in repeated compression. Data on dynamic stability of the specimens after aging are presented in Figure 6.

The stability of pliedup rubbers with breaker whether of natural rubber with carbon black, or of sodium-butadiene rubber, falls off sharply with prior thermal aging, nevertheless specimens with breaker of sodium-butadiene rubber have higher fatigue strength values after aging as compared with specimens with natural rubber breaker.

The addition of antioxidants to the breaker strip somewhat enhance the resistance of dynamic failure of pliedup rubbers, whether subjected or not to prior thermal aging (Figure 6 and Table VII).

The present method of assessing bond strength of pliedup systems in the form of cylindrical standard specimens, under repeated compression on a machine with constant initial loading (the MMS-1 machine) provided reproducible results in a large number of experiments.

Comparison of the resulting data on bond strength of tread breaker standard specimens with the data from tests on actual tire covers justifies the recommendation of our method for laboratory use.

METHODS FOR DETERMINATION OF RUBBER TO CORD BOND STRENGTH *

R. V. Uzina, L. S. Gromova, and S. A. Vasil'eva

In selecting methods for determination of rubber to cord bond strength it is necessary to consider the factors which are subject to variation in the system—the type of cord, the composition of the vulcanized rubber, or the composition of the impregnant. The selection (composition) of the methods of assessment of bond strength was carried out in the present study while keeping the type of cord and the rubber compositions constant; only the composition of the impregnant was varied.

Up to the present there has been no single laboratory method for evaluating rubber to cord bond strength for the determination of the service quality of rubber-fabric structures. The bond strength in such a system is assessed in the majority of cases by the use of a series of methods. The existing methods may be systematized according to the nature of the deformation (static or dynamic), the nature of the specimen (with single thread of cord or with cord fabric) and so on. We adopted the following classification of methods:

1). Determination of bond strength of a single thread of cord with the rubber;

2). Determination of bond strength of rubber to fabric model specimens.

Determination of bond strength of a single thread of cord with rubber is an exceptionally widely used type of testing in the rubber industry[1–4]. It is based either on the principle of stripping of a single thread of cord from the rubber under pressure, or on the principle of pull-out of a thread of cord from a rubber specimen.

Methods based upon the principle of stripping of a thread of cord from vulcanized rubber under pressure.—The method of determination of bond strength in static stripping of a single thread of cord from rubber during compression on a Schopper type dynamometer is used as an inspection method in the Soviet Union and elsewhere[2]. This method is characterized by adequate accuracy; to get bond strength readings with an experimental error not exceeding 10%, it is sufficient to carry out 6 parallel determinations. The shortcoming of the method is the subjective character of the observation of the end of the test (Figure 1).

The method of determination of bond strength by stripping of a single thread from the rubber in repeated compression on a Metallist works machine was developed by the Nauchno-Issled. Inst. Rezin. Prom. (Rubber Research Institute) and the Nauchno-Issled. Inst. Shin. Prom. (Tire Research Institute). This method of testing is characterized by its sensitivity to very slight variations in the constitution of the impregnating compositions surrounding the rubber and in the technology of the impregnation of the cord. A shortcoming

* Metody Opredeleniya Prochnosti Svyazi Reziny S Kordom. Translated by R. J. Moseley from '*Prochnost' Svyazi . . .*', **1954**, pages 184–95.

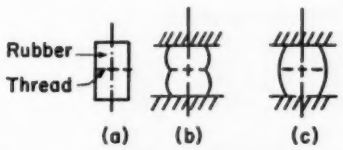


FIG. 1.—Specimen in static compression. a—Original unstressed specimen. b—Specimen compressed under a load. c—Specimen compressed under a load, after stripping of the thread of cord from the rubber (end of test).

of the method is the big scatter in the readings which makes it necessary to carry out not less than 20 duplicate determinations to get mean values with experimental error not exceeding 25% (Figure 2).

Methods based on the principle of pull-out of a thread of cord from the rubber.—In the literature there are numerous descriptions of testing rubber to cord bond strength by the method of pull-out of a thread from a specimen, particularly after prior fatigue of the specimen[1,3–6]. Of a large number of similar methods the best known are the methods of Korner and of H tests[1,3].

We checked on the method of Korner[3]. The determination of the rubber to cord bond strength was carried out after two hours heating of the specimens at 120° and subsequent fatigue on the Goodrich flexometer. It was ascertained that to obtain test results with an experimental error not exceeding 10% it was necessary to carry out not less than 10 parallel determinations (Figure 3). From the investigations it was ascertained that it is not possible to replace the inspection method of determination of bond strength by the thread pull-out method.

Parallel determinations of rubber to cord bond strength carried out in 1952 showed that the pull-out method cannot be used for the quality inspection of impregnations as this method does not react to fluctuations in the formula and in the technique of impregnation.

Bond strength determined by stripping a single thread of cord from rubber, kg	Bond strength, determined by the method of pull-out of a single thread of cord from rubber, after 2 h heating, kg/cm					
	Minimum	Maximum	Average	Minimum	Maximum	Average
	Viscose 13v			Cotton 9T		
Lower than 89.9	3.0	5.9	4.2	—	—	—
90.0 to 94.9	2.2	7.2	4.5	—	—	—
95.0 to 99.9	3.86	6.5	4.5	3.9	5.6	4.9
Above 100	2.9	5.8	4.6	1.8	6.0	3.5

Determination of bond strength of rubber-fabric specimens.—In recent years it has been rare to find a description of the method for determination of the bond strength of rubber-fabric specimens in non-Soviet literature.

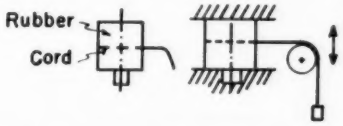


FIG. 2.—Specimen in repeated compression.

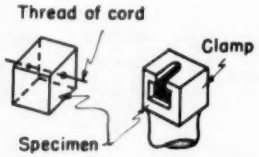


FIG. 3.—Specimen for pull-through of thread of cord.

We gave detailed consideration to the method for determination of bond strength between cord fabric and rubber during repeated flexing and during static stripping, a method which is widely used in experimental work.

In repeated flexing on a flexing machine it is necessary to carry out a large number of parallel determinations (more than 40) in order to get data with experimental error not exceeding 25%. As a result of the complication of the construction of the specimens testing presents considerable difficulties. Therefore, in spite of the good degree of agreement of the data obtained by this method with those of other methods, its use is not recommended.

Determination of bond strength by the method of stripping of rubber-fabric specimens likewise involves complicated preparation of the specimens, but gives somewhat greater accuracy of measurement (16 parallel determinations lead to error of not more than 10%). The principal shortcoming of this method is that it does not reveal changes in the formula and technique of impregnation and it does not agree with the data from other methods of testing (Figure 4).

Up to the present time there has not been a sufficiently accurate method of determination of the bond strength of model rubber-fabric specimens under dynamic deformations. One of the aims of our study was to provide such a method.

Our method of laboratory assessment of bond strength at the cord fabric-carcass rubber boundary is based on the principle of construction of a specimen proposed by Biderman and Reznikovskiĭ (see the article by M. M. Reznikovskiĭ, '*Prochnost' Svyazi*. . . .', p. 166) with normal arrangement of the cord fabric in relation to the platens of the machine (breaker fabric and Metallist works machine) (Figure 5).

The preparation of the specimens was carried out as follows. From a strip of carcass stock of thickness 7.2 to 7.5 mm there are cut out two circles of diameter 120 mm. A strip of cord of width 30 cm is covered with carcass stock (thickness of rubberizing on each side 1.6 mm). Increasing the gage of the rub-

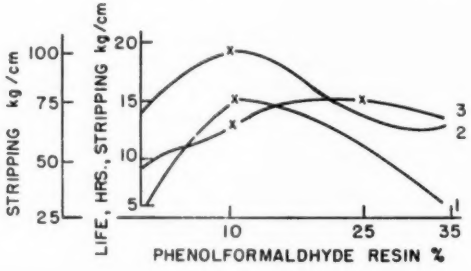


FIG. 4.

berized cord (4mm instead of 1.4 when the specimens are prepared for the flexing machine) is done so as to have a clear delineation of the character of the failure of the specimen. With smaller gage of rubberized cord (1.4 mm) failure during testing may take place at the rubber–rubber boundary layer, as a result of a poor bond of the rubbers which are being plied-up; the failure may be taken erroneously, as a failure of the cord-rubber system as a result of the high bond strength between them. Increasing the gage eliminates the possibility of error in the determination of the nature of the failure.

From the rubberized cord circles of diameter 120 mm are cut out. On a circle of carcass rubber there is placed a circle of rubberized cord and on top of this one more circle of carcass rubber. Vulcanization of the specimens is carried out in a circular "plunger" mold which is placed in an electric press.

The particular features of the testing method are as follows:

1) Vulcanization of the specimens in a plunger mold with constant applied pressure;

2) Simplicity of construction of the specimen, in contrast with the repeated flexing method in the flexing machine;

3) High accuracy in the results (error in measurement less than 25%) with a small number of parallel determinations ($n = 10$);

4) Simultaneous testing with shear deformation (breaker machine) and compression deformation (Metallist works machine) of small cubes cut from a single vulcanized specimen.

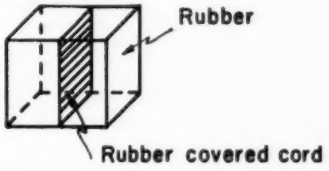


FIG. 5.—Model rubber-fabric specimen.

Selection of methods of determination of bond strength of cord and rubber.— Of decisive importance in the selection of a method of determination of bond strength at the cord-rubber boundary is the reproducibility and the fidelity with which this method reveals or simulates the principal deformations and stresses existing in the tire in service.

In order to show which of the methods for bond strength determination used at the present time represent the phenomena taking place in the tire at the cord-rubber boundary, we selected the five methods described above.

For our investigations we took 13V viscose cord, as being the most sensitive to changes in the formula and technique of impregnation. Different bond strength between the viscose cord and the rubbers was obtained as a result of using nonimpregnated cord, cord impregnated with the commercial impregnating[7] composition 50-u using wringing pressure during the period of impregnation (greater pressure gave a reduction in bond strength), and with impregnation of the cord with an aqueous solution of 89 resin, which raises the bond strength. The rubbers used were on a 100% SKB basis, used in the carcass of 260–20 tires. The results of laboratory determinations of bond strength between the

viscose cord and rubbers are shown in Figures 6–11; they show that the bond strength of viscose cord with rubber attained by different methods changes as a function of the formula and technological factors according to a single law.

Figure 6 shows the stripping face for a single thread of cord and rubber in static compression as a function of the treatment of the viscose cord. For I coating rubber based on 100% SKB for the first layers of the carcass was used; for II coating rubber based on 100% SKB for the following layers of the carcass was used. In Figures 7–11 and 15 the designations are as for Figure 6. Figure 7 shows the stripping of a single thread of cord from rubber in repeated compression as a function of the treatment of the viscose cord.

On comparison of the data obtained by the different methods it was demonstrated that there is a correlation between the bond strength determined from the static stripping of a single thread of cord from rubber in compression, repeated compression and repeated shear of rubber-fabric specimens (Figures 12–14).

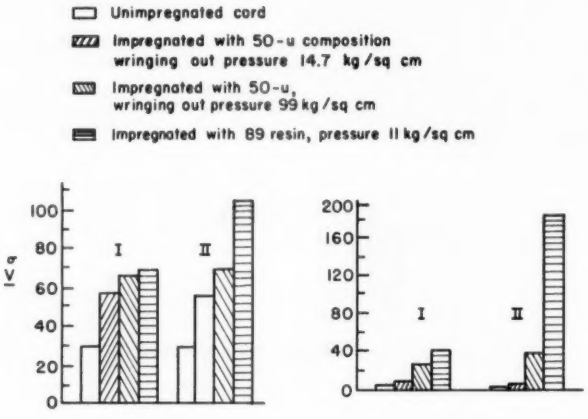


FIG. 6. FIG. 7.

All the methods of determination of bond strength were compared with the service life of casings in bench testing by the "carcass stripping" method. The method used previously for bench testing of tire casings did not afford the possibility of assessing bond strength between casing components (Figure 15). In this form of testing the carcass of the casing is under more severe conditions than in production testing. This method differs from that used previously by a 50% reduction in the internal pressure; a correction of the pressure was carried out after every 4 hours testing.

Comparison of the data on bond strength produced by laboratory methods of testing with the service life of casings in bench tests by the "carcass stripping" method showed that correlation of this last method is observed only with the methods of determination of bond strength in repeated shear and compression of rubber-fabric specimens and static stripping of the single thread of cord from rubber in compression (Figures 16–18). As a result of the fact that correlation exists between the methods of determination of bond strength in standard

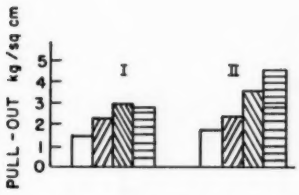


FIG. 8.—Pull-out of single thread of cord from rubber after heating, as a function of the treatment of the viscose cord.

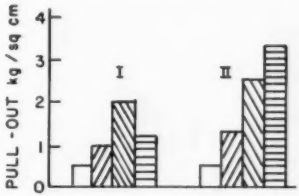


FIG. 9.—Pull-out of single thread of cord from rubber after fatigue, as a function of the treatment of the viscose cord.

rubber-fabric specimens in repeated shear and compression, it is possible to use one of these methods alone.

As a result of the work effected it is recommended that the rubber-cord bond strength be determined by the method of static stripping of a single thread of cord from rubber during compression and by the method of testing of standard rubber-fabric specimens in repeated shear.

Particular interest attaches to the method of determination of bond strength by stripping of a single thread of cord from rubber in repeated compression. This method of testing is not correlated with the other laboratory methods and with the method of bench testing the casings on account of the fact that it is exceptionally sharply affected by very small changes in the formula and technique of impregnation (Figure 7). It is recommended that the method be used in the case of quite small changes in the formula of the impregnating compositions and of the rubbers, in the technique of impregnating, and in the treatment of the cords.

On studying the bond strength at the cord-rubber boundary, with different compositions of rubber and with the impregnation layer unchanged we can see that the other methods give better agreement with bench tests, but this question calls for separate consideration.

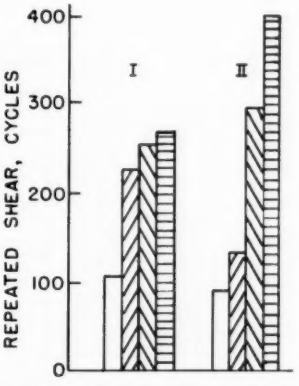


FIG. 10.—Repeated shear of rubber-fabric specimens as a function of the treatment of the viscose cord.

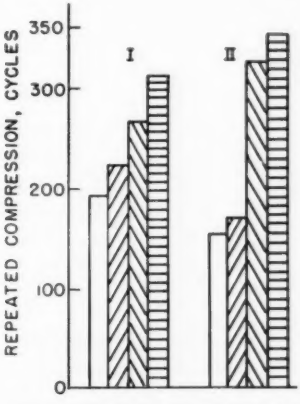


FIG. 11.—Repeated compression of rubber-fabric specimens as a function of the treatment of the viscose cord.

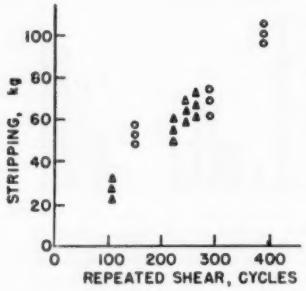


FIG. 12.—Comparison of stripping data of single thread of cord from rubber during static compression with the data for repeated shear of rubber-fabric specimens.

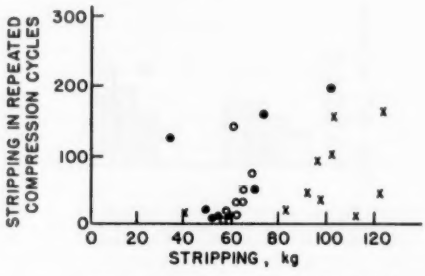


FIG. 13.—Comparison of stripping data of single thread of cord from rubber during repeated compression with data for stripping of a single thread of cord from rubber in static compression.

CONCLUSIONS

1. The following methods of determination of bond strength of a single thread of cord with rubber were studied: a) the method of static stripping of a single thread from rubber in compression; b) the method of stripping a single thread of cord from rubber in repeated compression; c) a method based upon the principle of pull-out of a thread of cord from rubber after heating and fatigue.

2. A method is developed for determination of bond strength of rubber-fabric specimens in repeated deformation by shear and compression.

3. Five methods of determination of bond strength of rubber with cord are compared:

i) stripping of a single thread of cord from rubber in static compression;

ii) stripping of a single thread of cord from rubber in repeated compression;

iii) pull-out of a single thread of cord from rubber before and after fatigue;

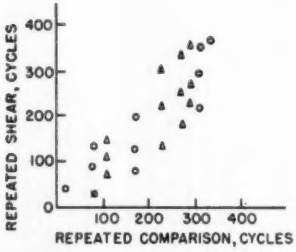


FIG. 14.—Comparison of data for repeated shear with data for repeated compression of rubber-fabric specimens.

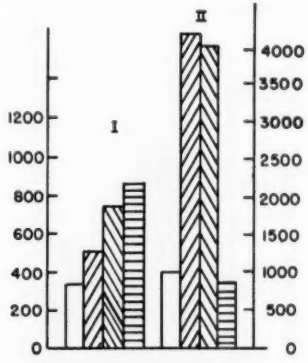


FIG. 15.—Service life (Km) of casings in bench tests. I—testing by the "carcass stripping method". II—testing by production method.

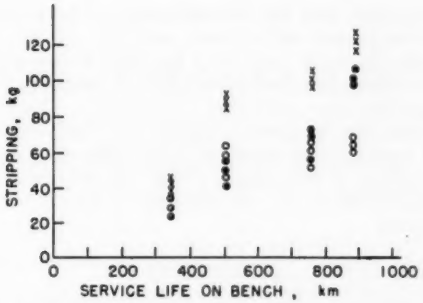


FIG. 16.—Comparison of stripping data of a single thread of cord from rubber during static compression with data for service life of casings in bench tests by the "carcass stripping" method.

iv) testing of standard rubber-fabric specimens in repeated shear; and

v) testing of standard rubber-fabric specimens in repeated compression.

4. A correlation is demonstrated between the data for bond strength obtained by the method of static stripping of a single thread of cord from rubber during compression, the method of repeated compression of rubber-fabric specimens and the method of repeated shear of rubber-fabric specimens.

5. The five methods of determination of bond strength are compared with the service life of tire casings in bench testing by the "carcass stripping" method.

6. A correlation is demonstrated between the service life of casings in bench testing and the bond strength of cord with rubber with the following methods of testing; static stripping of a single thread of cord from the rubber in compression, repeated shear and compression of rubber-fabric specimens.

7. It is shown that a correlation exists between the methods of determination of bond strength of standard rubber-fabric specimens in deformation by repeated shear and by compression. On this basis one of these methods may be used for testing.

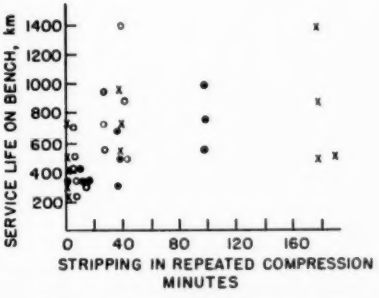


FIG. 17.—Comparison of data of service life of casings in bench tests by the "carcass stripping" method with data for stripping the single thread of cord from the rubber in repeated compression.

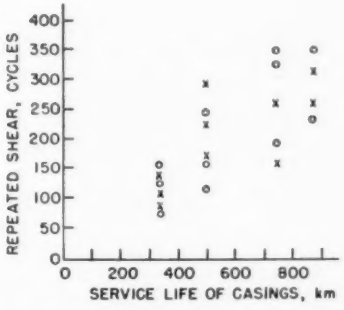


FIG. 18.—Comparison of data for repeated shear of rubber-fabric specimens with data for service life of casings in bench tests by the "carcass stripping" method.

8. It is recommended that the determination of the bond strength of the cord with rubber be carried out by two methods: by the method of static stripping of a single thread of cord from the rubber during compression and by the method of testing standard rubber-fabric specimens in repeated shear or in compression.

9. Where it is necessary to show the influence of small differences in formula and technique of impregnation upon bond strength it is recommended that there be used the method of stripping of a single thread of cord from the rubber since this is sharply sensitive to very small changes in the formula and technique of impregnation.

REFERENCES

[1] Lyons, W., Nelson, M., and Conrad, C., *India Rubber World* **114**, 213 (1946).
[2] Lessig, E., and Compton, J., RUBBER CHEM. & TECHNOL. **19**, 223 (1946).
[3] Carner, E., and others, *Trans. Inst. Rubber Ind.* **24**, 284 (1949).
[4] Moakes, R. C. W., *India Rubber J.* **121**, 719 (1951).
[5] Lyons, W., *Rubber Age* (N. Y.) **68**, 567 (1951).
[6] Pittman, I., and Thornley, E., *Trans. Inst. Rubber Ind.* **25**, 116 (1949).
[7] Uzina, R. V., "Collection Production and Use of Synthetic Latexes", Goskhimizdat, 1953, p. 61.

APPLICATION OF STRAIN GAGES TO THE STUDY OF (TIRE) CORD AT HIGH ELONGATION RATES *

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The modern automobile and airplane tire represent complex rubber-fabric construction which must function under a variety of conditions of road surface, loading, temperature, type of vibration, etc. One of the basic construction elements of any modern tire, as important as the rubber, is the carcass, the quality of which determines the durability of a tire to a considerable degree. At the present time the prevailing carcass materials are the synthetic and natural fibers, viscose rayon, caprone and cotton. (Translator's note: caprone is thought to be a Nylon 6 type of fiber.) The quality of the materials designed for the preparation of the carcass is determined by the standard laboratory methods used for single cords (breaking force in kg, breaking length in km, relative elongation at break, resistance to frequent stretching or bending deformation). The last type of test is seldom applied in factory laboratory practice. It should be noted that the cords in a tire are subject to different types of vibrational deformation. Among the most likely deformations to occur are stretching and compression flexing under different loads, and deformation caused by single or multiple impacts.

At the present time the efficiency of tire cord under stretching or bending flexing is evaluated by the number of cycles necessary for failure of the sample of cord. The resistance of a cord sample to a suddenly applied load in the longitudinal or transverse direction is evaluated by the quantity of work or energy of breaking. This is determined by the difference in the angle of upward flight of the free falling pendulum of an impact machine with and without the cord sample in the path of the pendulum.

The work in this case can be determined by the following formula:

$$A = C\,(\cos\theta_0 - \cos\theta_1), \tag{1}$$

where A = work of breaking cord, kg cm. C = pendulum constant depending on the weight G of the head and the distance R from the axis of suspension. G is expressed in kg, R in cm. θ_0 = angle of upward flight of pendulum in free fall. θ_1 = angle of upward flight of pendulum after breaking cord.

The quantity of work of breaking the sample is also numerically equal to the area under the stress-strain curve at constant rate of stretching. Analytically, this is expressed by the formula:

$$A = \int_{\epsilon 0}^{\epsilon_m} P\,d\,\epsilon \tag{2}$$

where P = effective force in kg as a function of the amount of deformation ($P = f(\epsilon)$). ϵ_m = deformation at break.

* Translated by Theodor Tarasjuk, Katherine and Willard P. Tyler for Rubber Chemistry and Technology from *Kauchuk i Rezina* **17**, No. 9, 12–16 (1958).

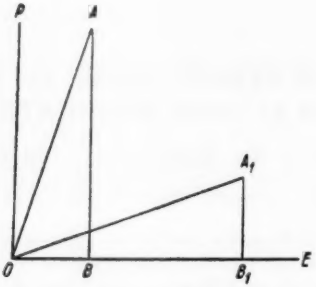


FIG. 1.—Diagram illustrating the change in character of the stress-strain curve and the value of work of breaking as a function of the speed of stretching.

Thus, if a stress-strain curve at a given rate of elongation is available, the work of breaking can be determined with a planimeter. In addition, the work of breaking can be determined without having the complete stress-strain curve by the method of approximate integration[1]. For this it is necessary to know the value of stress and elongation at break and the stress values at a few intermediate elongations.

In the case of tests of cord in which the elongation rate is low, intermediate elongation values are not difficult to obtain. However, they are difficult to obtain if the elongation rate is several meters per second.

The literature[2,4,5,6,7,10] describes several instruments for testing textile materials at high deformation speeds. Early instruments include the pendulum and vertical impact machines which are widely used in experimental practice. Later methods of recording longitudinal breaking at high speed include high speed motion pictures and optical methods of recording.

It should be noted that the methods of testing, with the exception of optical recording, provide practically no possibility of determining intermediate values on the stress-strain curve. Therefore the work of breaking is determined by

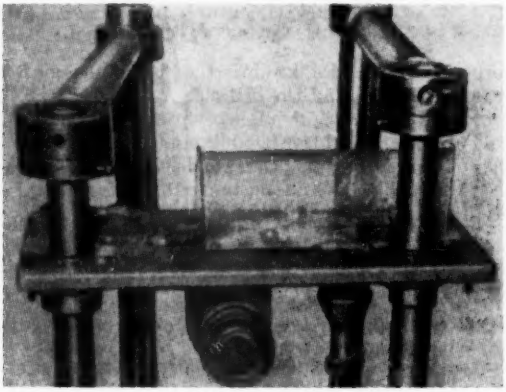


FIG. 2.—General view of transducer.

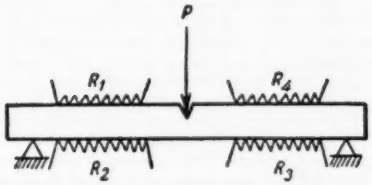


FIG. 3.—Diagram of beam with gages cemented to it.

Formula (1) by experimental testing on an impact machine or by some other cumbersome method[8,9]. Besides, the limitations of the impact machine with respect to speed of deformation should be emphasized. Meanwhile, it is obvious that for complete characterization of a tested material at different rates of deformation it is necessary to know both the value of the breaking energy and the nature of the stress-strain curve. The need for obtaining the stress-strain curve can be illustrated by the following scheme[11] (Figure 1). If two identical samples are stretched at different rates it will be found that the work of breaking of the samples (A_1 and A_2) is equal but the nature of the stretching is different. For sample A_1, strength is the main factor; for sample A_2, the amount of elongation.

Therefore, in order to more completely evaluate the change of properties of material at high deformation rates it is necessary to know the stress-strain curve as well as the breaking energy. It was shown[10] that on testing cord on the pendulum impact machine, the time of deformation was hundredths of a second. Naturally the recording of such a rapid process can not be achieved with the conventional mechanical recorders.

We attempted to record the curve of longitudinal stretching of cord at elongation rates of 1.5 m/sec. In this case the test lasts for 1×10^{-2} to 2×10^{-2} sec. Apparatus has been described[3] on which the stress-strain curve was recorded by means of an oscilloscope, EO-4, and later by a specially constructed oscilloscope with a persistent image. The principle of this apparatus was used as the basis for the mechanical part of our apparatus. In our work the electromagnetic oscillator, MPO-2, was used. A wire of given resistance was used to convert mechanical energy into electrical energy. The construction of the transducer was developed and carried out in the laboratory of the NIIShP. It should be mentioned that the strain gage was used for recording only one parameter, force. For recording the other parameter, deformation, a transmitting slide wire was used.

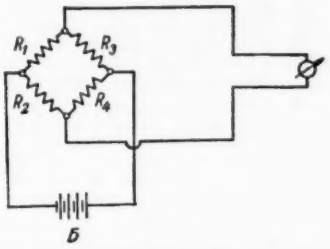


FIG. 4.—Wiring diagram of gages.

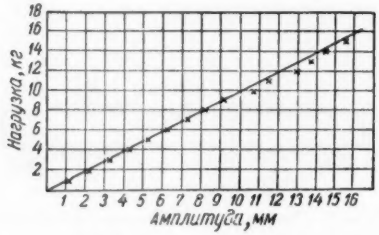


FIG. 5.—Calibration curve for strain gage. Abscissa: amplitude mm. Ordinate: load, kg.

Thus a record of the entire process of stretching the cord at a given speep can be obtained in the form of simultaneous curves on film. Figure 2 is a complete view of the transducer.

On a steel beam resting on two triangular supports are adhered four wire strain gages with a nominal resistance of 150 ohms. The length of the wire strain gage is 25 mm. The material is tempered, and of constant diameter, 30 μ. The gages are attached by means of adhesive BF-2. Figure 3 shows the beam with gages attached to it. The action of force P causes a deflection, the amount depending on the force P, the material and the size of the beam. Consequently the upper surface of the beam is compressed and the lower surface is extended. Thus the resistance of the upper gages, R_1 and R_4 decreases by some value ΔR while the resistance of gages R_2 and R_3 increases by a value ΔR_1. From these considerations, and also from the desire to obtain maximum sensitivity from the gages, the wiring diagram shown in Figure 4 is the most desirable. This scheme provides sensitivity of the gage of the order of 100 g/mm.

The strain gage assembly is placed on the triangular support and firmly fastened to a massive steel plate. The plate is firmly attached to vertical legs by means of special fastening sockets. In this manner sufficient rigidity of the entire apparatus is obtained. The ends of the beam are prevented from sliding off the supports, after the cord is broken, by special stops. The grip is connected with the beam by means of a coupling rod screwed into a special stirrup which rests in the triangular notch in the center of the beam. For sturdy fastening of the cord in the grip a conical bushing is provided which will secure the cord when the bushing is turned. During this time the stirrup is

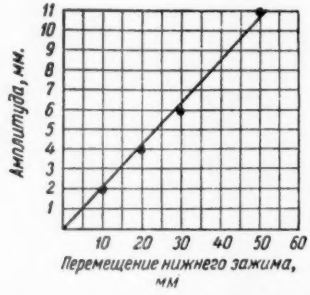


FIG. 6.—Calibration curve for deformation gage. Abscissa: Displacement of lower clamp, mm. Ordinate: Amplitude, mm.

lifted off the beam by 0.2–0.5 mm. After the cord is secured, the strirup is lowered into place on the beam. The sagging of the beam caused by the loading existing at the moment the thread breaks is dependent on the speed of stretching and varies from 1.2 to 1.4 $\times$ 10^{-2} mm. The power supply for the strain gage is a four channel amplifier. The amplifier provides 6–6.5 V with a resistance of no more than 200 ohms. The carrier frequency reaches 500 kc.

The voltage necessary to balance the bridge is fed to the amplifier. Thus, changes in force acting on the beam result in changes in the output of the amplifier. The changes in current output are recorded on 35 mm film through the use of an electromagnetic oscillator having the following characteristics: Type IV; natural frequency of vibration in air, 300 kc; sensitivity, 100 mm/ma on the film and 4.00 mm/ma on the screen; resistance 6.0 ohms; maximum amplitude of current, 25 ma; maximum deflection on screen, 100 mm. (Translator's Note: This apparatus is apparently a mirror galvanometer, possibly a string galvanometer.)

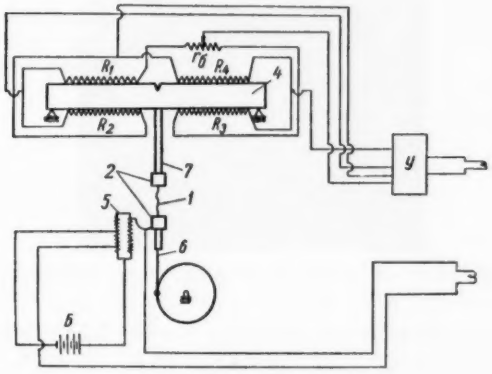


FIG. 7.—General diagram of instrument.

To avoid distortion of the record of the process the carrier frequency must be 5–10 times as great as that of the process and the natural vibration frequency must be ten times as great as that of the process. In the tests described the frequency of the process did not exceed 5 kc.

The described transducer had good stability as demonstrated by reproducibility on periodic calibration. The stability was guaranteed by shielding all connecting leads, and also by the nature of the circuit itself which permits compensation for temperature fluctuation.

Before work was started, the transducer was calibrated to determine the relation between the applied force and the output of the amplifier. The calibration curve is shown in Figure 5.

A transmitting slide wire is used to measure the deformation. The slide wire is one arm of a bridge. The sliding contact is fastened in such a manner that at the upper position of the lower clamp no current flows. When the clamp is lowered during stretching of the sample the ratio of bridge arms is changed. The power supply for the transmitting slide wire is a 6–7 volt battery. A 6–8 volt battery would be a more desirable source of power. As with

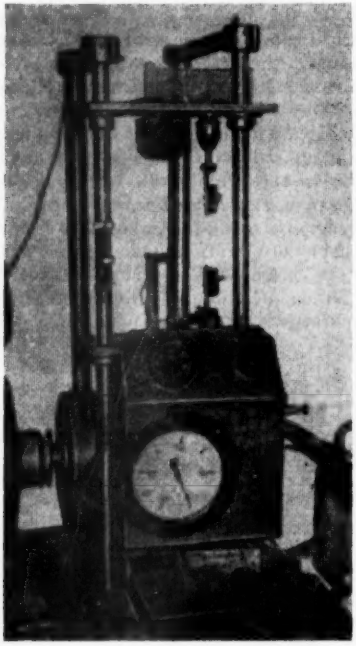


FIG. 8.—General view of instrument for testing cord by stretching at different speeds.

the strain gages, calibration was carried out to determine the relation between motion of the clamp and the current flowing in the bridge circuit. The calibration curve is shown in Figure 6. The schematic plan of the apparatus for stretching cords at different speeds is shown in Figure 7 and a picture of the entire assembly is shown in Figure 8.

On the instrument described a series of tests of samples of cords of caprone, of imported fiber (terylene) and some specially prepared caprone cord. The fibers for the latter samples were subjected to boiling water for 3 hours.

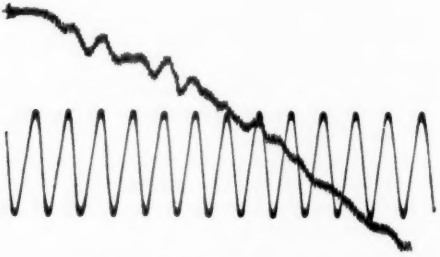


FIG. 9.—The type of oscillogram obtained.

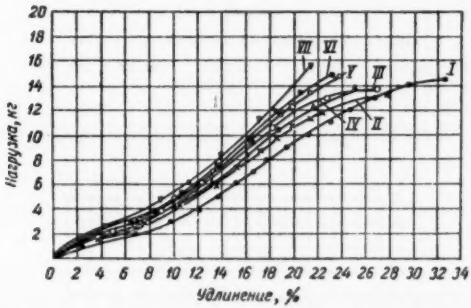


FIG. 10.—Stress-strain curves of a series of caprone cords stretched at different rates. Abscissa: elongation, %. Ordinate: load, kg. *I*—0.005 m/sec; *II*—0.041 m/sec; *III*—0.082 m/sec; *IV*—0.35 m/sec; *V*—0.505 m/sec; *VI*—0.84 m/sec; *VII*—1.5 m/sec.

The type of oscillogram obtained is shown in Figure 9 and stress-strain curves calculated from the oscillograms are shown in Figures 10, 11, and 12. The time for breaking was determined by the formula[12]:

$$K_t = \frac{n}{mf} \tag{3}$$

where K_t = time
n = number of cycles on oscillogram
m = number of scale divisions
f = frequency per scale division.

The accuracy and reproducibility of results were entirely satisfactory both as to breaking load and elongation at break. The average error of 25–30 replicate tests was about 4% (4.17–4.3%).

It can be seen from Figure 10 that an increase in rate of stretching leads to some increase of breaking load and to a sharp decrease in elongation at break. The modulus of the cord increases with increased stretching speed.

This pattern of changes of mechanical properties is also found for the specially prepared samples and for terylene (Figures 11 and 12). Evidently such a change in the nature of the stress-strain curves as a function of speed of stretching can be related to the relaxation process.

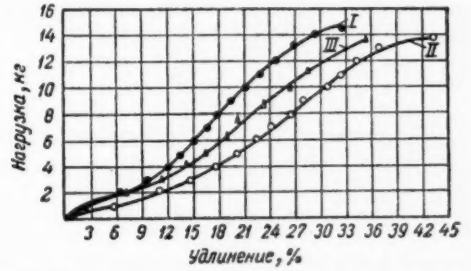


FIG. 11.—Stress-strain curves of caprone cord treated in boiling water. Abscissa: elongation, %. Ordinate; load, kg. *I*—0.005 m/sec; *II*—0.005 m/sec (boiled); *III*—1.5 m/sec (boiled).

TABLE I

BREAKING WORK AT DIFFERENT RATES

Rate of deformation, m/sec	0.041	0.082	0.35	0.505	0.84	1.5
Time of stretching, sec	3.3091	0.9175	—	—	—	0.0245
Work of breaking, kg cm						
Untreated						
Caprone	24.2	24.3	21.0	20.8	19.1	18.5
Terylene	9.05	—	—	—	—	6.25

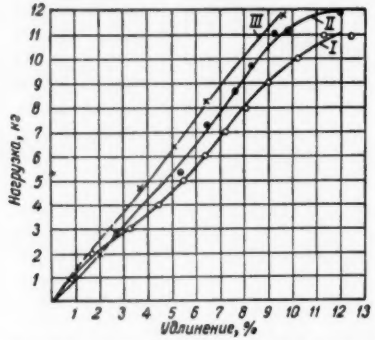


FIG. 12.—Stress-strain curves of terylene stretched at different rates. Abscissa: elongation, %. Ordinate load, kg. *I*—0.005 m/sec; *II*—0.041 m/sec; *III*—1.5 m/sec.

The work of breaking at different stretching rates was obtained from the stress-strain curves (Table I).

In conclusion, it should be noted that the developed method of recording the stress-strain curve is adequately simple and can be used for stretching tests on elastic materials with large or small elongation at break and also on other materials. The necessary cross section of the beam should be selected on the basis of the strength of the materials being tested. On this apparatus no distortion of the record will be obtained below a speed of 5 m/sec.

CONCLUSIONS

1. A new simplified method of recording the stress-strain curve of elastic materials using strain gages was developed and tested.

2. It was found that there is a substantial influence of rate of deformation on the character of the stress-strain curves of the samples tested.

3. It was established that the work of breaking the tested samples decreases with increasing speed of stretching.

REFERENCES

[1] Zotikov, "Strength of Cotton Fiber on Stretching. Methods for the Determination of the Fundamental Properties of Cotton Cord", NITI, 1933.
[2] Lyons, W. J., and Prettyman, I. B., *Textile Research J.*, **23**, 917 (1953).
[3] Zhurkov, S. N., Tomashevskii, T. P., and Sanfirova, T. P., *Zhur. Tekh. Fiz.* **23**, 933 (1953).
[4] Springer, A., *Faserforsch. u. Textiltech.* **6**, No. 2, 76 (1955).
[5] Meredith, R., *J. Textile Inst.* **45**, T30 (1954).
[6] Schiefer, H. F., Appel, W. D., Krasny, J. F., and Richey, G. G., *Textile Research J.* **23**, 489 (1953).
[7] Stone, W. K., Schiefer, H. F., and Fox, G., *Ibid.* **25**, 520 (1955).
[8] McCrackin, F. L., Schiefer, H. F., Smith, J. C., and Stone, W. K., *Ibid.* **25**, 529 (1955).
[9] Smith, J. C., McCrackin, F. L., and Schiefer, H. F., *Ibid.* **25**, 701 (1955).
[10] Rogovina, A. A., and others, *Zhur. Tekh. Fiz.* **26**, 2684 (1956).
[11] *Ibid.* **26**, 2690 (1956).
[12] Raevskii, N. P., "Methods of Experimental Research on the Mechanical Parameters of Machines", published by AN SSSR, 1952.

ROTARY POWER LOSS MACHINE*

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INTRODUCTION

Rubberlike polymeric materials, particularly in the technical form when compounded with carbon black, are imperfectly elastic and the associated energy loss is of considerable practical significance.

In some applications a high energy loss is of value to provide high damping, but in many cases and particularly in tires, the temperature rise due to the losses may be a limiting operational factor.

The losses cause the tire to exhibit rolling resistance which, in the case of solid tires, can be related accurately to the modulus and resilience of the rubber.

An analysis of this system has been carried out by Evans[1], while Tabor[2] has considered the case of rigid cylinders and spheres rolling on flexible rubber surfaces.

In the case of pneumatic tires the composite nature of the construction of fabric and rubber and the complex system of strain distribution make the calculation of rolling resistance from polymer properties extremely complicated.

In order to approach this problem it is necessary to know the modulus and resilience of the materials used over a very wide range of temperature and a range of amplitude of deformation and of frequency. The required temperature range may be from $-60°$ C to above 200° C, but the frequency range over which appreciable amplitudes are involved does not extend beyond approximately a thousand cycles per second while the amplitude of deformation does not exceed 50 per cent.

In order to investigate adequately the many possible combinations of polymers and compounding systems, the values of resilience and modulus are required over the above range of conditions, and various instruments have been described which measure some or all of these properties.

The rebound pendulum[3] was one of the earliest instruments and is widely used for the measurement of resilience because of its inherent simplicity of operation and high accuracy, but as normally operated at a fixed temperature does not provide sufficient information for evaluation of materials for use in tires. This type of instrument also is not well suited for determination of modulus owing to its single cycle method of operation.

The vibrator type instruments[4,5,6,7] give more complete information but normally demand a high degree of skill in their operation and in the interpretation of results and are more suited to research than routine work.

The machine to be described is a robust instrument capable of measuring energy loss, modulus and resilience, over a wide range of temperature and amplitude. As in practice the range of frequency is limited, measurements involving variation in frequency are less important than variation in tempera-

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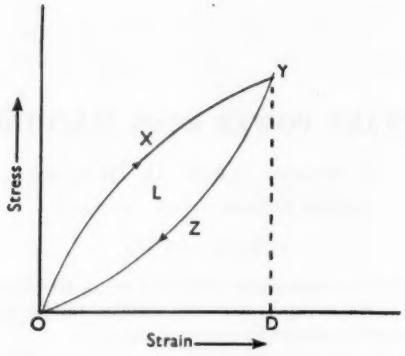


FIG. 1.

ture in routine measurements, so for reasons of simplicity a fixed frequency is used.

The machine consists in principle of a rubber wheel running on a rigid drum and the energy loss and dynamic deflection of the rubber are measured directly. This form of sample has the advantage of providing a deformation cycle parallel to that experienced by a rolling tire, but essentially it is a test specimen from which values of rubber properties can be obtained by calculation. The modulus and its variation with amplitude is calculated from the deflections while the resilience is obtained from the measured energy loss and a calculation of the energy stored in the deflected portion of the sample.

PRINCIPLE OF RESILIENCE MEASUREMENT

When a material is deformed a stress-strain relationship during deformation is given by the curve OXY in Figure 1, whereas when the strain is removed the curve YZO is obtained. The areas underneath these curves to the strain axis represent energies, so that the energy "A" used in deforming the material is represented by $OXYDO$, and that returned on releasing the strain is represented by $OZYDO$. Thus, if the material is taken through a deformation cycle O to Y and back to O an amount of energy $L = OXYZO$ has been lost. This energy

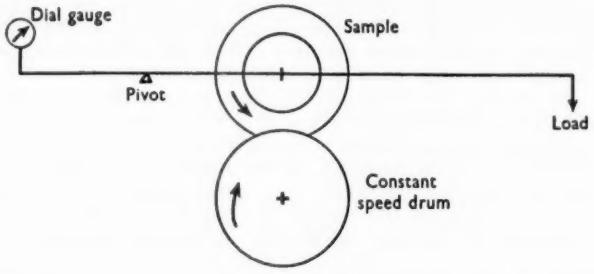


FIG. 2.

appears as heat in the sample. The term resilience has been established for the pendulum as a measure of the relative energies and the same definition is used for results from this machine, i.e.—

$$\text{Resilience} = \frac{\text{Energy returned per deformation cycle}}{\text{Energy input per deformation cycle}} = \frac{\text{Input} - \text{Loss}}{\text{Input}} = \frac{A - L}{A}$$

The principle of operation is shown in Figure 2. The sample under test is in the form of a solid annulus of rubber molded on to a metal center and is free to rotate on a steel drum running at constant speed. The sample is deflected under an applied load and the deflection of the sample is measured. The drum is driven by a constant speed motor of which the stator is suspended in ball races so that the energy absorbed in the sample can be obtained from the angular deflection of the stator.

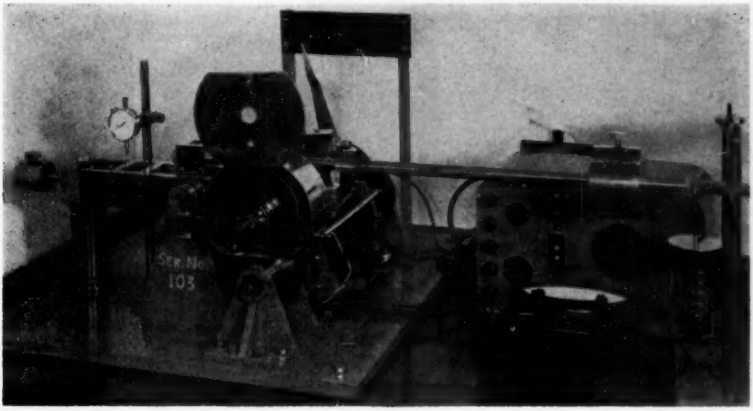


FIG. 3.

The speed used is 5.5 rps and the frequency of deflection corresponds to approximately 30 mph on the road. The maximum strain is in the range 10 to 25 per cent.

DESCRIPTION OF MACHINE AND SAMPLE MOUNTING

Figure 3 gives the general arrangement of the machine and the sample is shown in more detail in Figure 4. It is the form of a rubber annulus of square cross section, 4 inches external diameter, $2\frac{1}{2}$ inches internal diameter and $\frac{3}{4}$ inch wide, molded on to a metal center which can be of two types:

(*a*) A grooved metal center. In this type, the rubber is secured mechanically to the center by undercut grooves in the metal arranged both circumferentially and parallel to the axis of the wheel.

This center can be used at loadings up to 20 kg, and at temperatures up to 150° C. Above these values a certain amount of movement and abrasion may occur at the rubber-metal interface, particularly with soft samples.

This type of center is found to be quite satisfactory for normal test conditions and the sample is prepared by straight-forward molding methods and is easily stripped after test leaving the center ready for further use.

(*b*) A plain metal center. In this type the rubber is brass or chemically bonded to the metal to prevent any movement at the rubber-metal interface and is of particular value at loads above 20 kg on the sample.

The disadvantage is that the center must be specially prepared, and after test the rubber has to be removed by special techniques.

The sample is carried on a free-running shaft and is secured to it by a peg and hole arrangement at the rear of the metal center. Associated with this system is an eccentricity correction system to be described below.

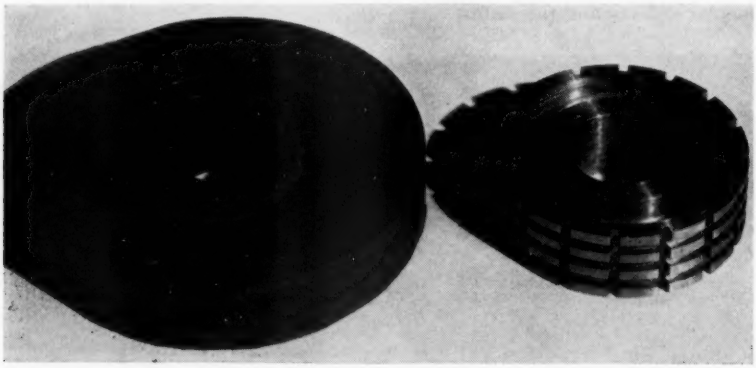


FIG. 4.

The shaft is carried on a subframe which is damped by means of an oil dashpot. By balancing the subframe the sample is made to run on the drum with zero deflection. This gives the zero positions for deflection measurements and for the energy loss measurement which is obtained from deflection of the motor stator. Load is applied to the sample by means of a lever, pivoted at the same center as the subframe. Weights can be hung on the end of the arm to give several set values of load, while a sliding weight enables subdivisions between these values to be obtained. The range of load on the sample is from 5 to 40 kg.

As the outer diameter of the rubber may be slightly eccentric with respect to the shaft, due to inaccuracy in molding, this may give rise to fluctuations on the deflection gage. These can be reduced to a minimum by rotation of an eccentric bush placed between the sample center and the shaft which is machined eccentric at the point supporting the sample. The maximum eccentricity which can be corrected is 0.5 mm and correction is carried out by rotating the bush and then pegging the sample to a disc on the shaft.

TEMPERATURE CONTROL AND MEASUREMENT

The sample is surrounded by an oven so that its temperature can be raised above room temperature by external heat as well as by energy dissipated within the sample. The rate of rise of temperature is controlled by a variable voltage transformer which supplies the heater. The maximum temperature attainable is over 200° C.

For measurements below room temperature the oven can be replaced by a container holding solid CO_2. The sample is first cooled to below the lowest temperature desired, e.g., in a refrigerator or by packing in solid CO_2 and readings taken as the sample warms up.

The temperature of the sample is measured by means of an iron-constantan thermocouple threaded through the center of the sample after it has been molded. The thermocouple leads are brought out through rotating point contacts of the appropriate metals at either end of the shaft so that continuous temperature measurement is obtained. These contacts are lubricated with graphite grease. The stationary contacts are mounted on arms which can be swung outwards to enable the sample to be mounted on the shaft and during observations held against the rotating points by spring tension.

MEASUREMENTS OF ENERGY LOSS AND SAMPLE DEFLECTION

The constant speed steel drum is driven by a one-tenth hp, 3-phase, synchronous motor with a built-in gear box giving a final shaft speed of 5.5 rps. The stator is suspended on ball races carried on the two shafts which are in line.

A single phase motor could be substituted for the 3-phase synchronous motor but the latter is preferred for its constant speed.

When energy is absorbed by the sample the reaction torque on the motor causes the stator to swing to a poistion such that the additional motor torque is balanced by the gravitational torque of the displaced mass of the motor-gearbox system. The energy loss in the sample is determined by the position of a pointer attached to the motor and moving over a fixed scale, initially calibrated by a band brake on the steel drum. Zeroing of the pointer on the scale is effected by a fine screw control fixed to the side of the motor body. Losses such as friction in bearings, air drag on the sample, and losses in the gear and motor system, either do not affect the system or are allowed for by adjusting the scale to zero when the sample is rotating but is not deflected.

The only uncompensated loss is the increase in bearing friction as the load is applied and this is minimized by careful maintenance of the bearings. This loss can be checked by running a solid steel disc in place of the rubber sample.

The sensitivity of the energy loss measurement system can be varied by raising the center of gravity of the system by adding weights to a center pillar attached to the stator.

Any random fluctuations of the stator position are damped by an eddy current brake, a $\frac{1}{4}$-inch thick copper plate attached to the stator and located between the poles of a permanent magnet.

The sample and drum are nominally of the same diameter, but owing to small variations in the sample diameter and to the tangential drag forces arising from energy loss, which has the effect of displacing the center of pressure in the rubber from the line joining the axes of the drum and sample, there may be a slight difference between drum and sample revolutions which rarely exceeds 1 per cent. This can be measured by a stroboscope disc and neon lamp on the

rear of the sample shaft and so arranged that the per cent error from the synchronous speed is observed as a direct reading.

Any frequency error in the mains supply will alter the motor speed but this does not influence the accuracy of the results significantly.

For each measurement, readings are taken of energy loss from the stator deflection, the dial gage deflection reading and the temperature. Readings are taken at approximately 5° C intervals up to the maximum desired and also during cooling if required. Approximately 1 hour is required to complete a test. To avoid local overheating of the surface of the sample the machine is not stopped during the test run; chalk may be applied to the sample surface if excessive tackiness develops due to surface oxidation. By taking readings at a series of differing loads the modulus-amplitude relationship is obtained from the deflections of the sample. The deflection dial gage is adjusted to zero by removing the load from the sample at suitable time intervals to correct for dimensional changes due to thermal expansion of the rubber, etc.

CALCULATION OF RESULTS

Dynamic modulus.—In Figure 5 the sample is deflected to the form ADC by the drum.

Let P = applied load.
f = stress on element dx.
d = maximum deflection of sample.
y = deflection of element dx.
$2c$ = chord.
F = "Form Factor" of sample.
r = external radius of sample and drum = 2 inches (5.08 cm).
r_1 = internal radius of sample and drum = $1\frac{1}{4}$ inches (3.19 cm).
h = depth of sample $(r - r_1)$ = $\frac{3}{4}$ inch = 1.9 cm.
b = width of sample = $\frac{3}{4}$ inch = 1.9 cm.
s = strain = $\frac{y}{h}$
E = modulus.
n = index relating modulus to strain.

Under the conditions considered, the frequency of deformation is constant, but the amplitude varies as the element dx passes through the deflection cycle.

According to Evans[1] $P \alpha d^1$ and this is the theoretical value for a material of which the modulus is independent of the amplitude but our experimental data and also that of Meij and Amerongen[8] and Fletcher and Gent[9] show that there is a dependence of modulus upon amplitude.

The relationship of load to deflection is in the general form $P \alpha d^{1-n}$ from experimental plots of log P versus log d, where n varies with the material and has a value between 0 and 0.5, approximately. This can be expressed by considering the modulus to be related to amplitude by the form $E(y) = E\left(\frac{y}{h}\right)^{-n}$. While recognizing that this form is only a second approximation, it is closely obeyed by the results of the above authors.

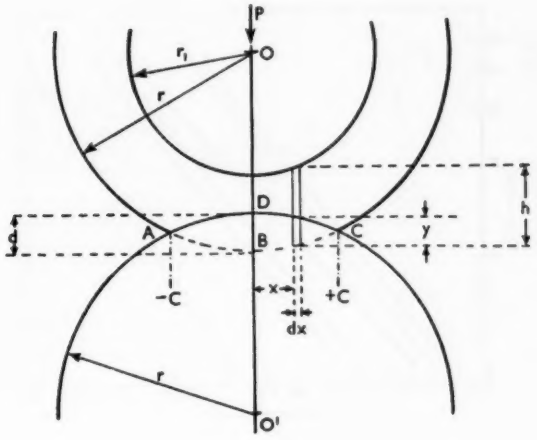


FIG. 5.

Let

$$E(y) = E\left(\frac{y}{h}\right)^{-n}$$

$$f = E\left(\frac{y}{h}\right)^{-n} s = E\left(\frac{y}{h}\right)^{1-n}$$

Hence the load carried by the element will be

$$dP = Ffbdx$$

$$dP = FE\left(\frac{y}{h}\right)^{1-n} bdx \tag{1}$$

$$P = \int_{-c}^{+c} dP = \int_{-c}^{+c} FE\left(\frac{y}{h}\right)^{1-n} bdx$$

$$= \frac{FE\,b}{h^{1-n}} \int_{-c}^{+c} y^{1-n}\,dx$$

assuming h is constant over the range $+c$ to $-c$.

From the simple geometry of the deformation of the sample by the drum

$$y = 2\sqrt{(r^2 - x^2)} - 2r + d$$

$$\therefore P = FE\frac{b}{h^{1-n}} \int_0^d y^{1-n} \sqrt{\frac{r}{d}} \left[\frac{1 - \left(\frac{d-y}{2r}\right)}{\sqrt{1 - \frac{y}{d}}\sqrt{1 - \left(\frac{d-y}{4r}\right)}} \right] dy$$

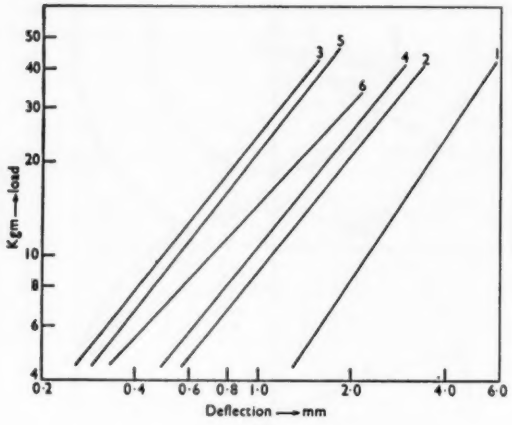


FIG. 6.

1. Natural rubber gum.
2. Natural rubber + 50 HAF.
3. Neoprene + 50 HAF.
4. Krynol + 50 HAF.
5. Hycar + 50 HAF.
6. Butyl + 50 HAF.

For values of $d < 0.5$ cm, $\frac{d-y}{2r} \ll 1$ for an error in P of less than 1 per cent.

$$P = FE\frac{b}{h^{1-n}}\sqrt{\frac{r}{d}}\int_0^d \frac{y^{1-n}}{\sqrt{1-\frac{y}{d}}}dy$$

$$\therefore P = FE\frac{b}{h^{1-n}}\sqrt{r}\,d^{\frac{1}{2}-n}\quad k^n \tag{2}$$

or

$$E = \frac{Ph^{1-n}}{F\,b\,\sqrt{r}\,d^{\frac{1}{2}-n}\quad k^n} \tag{3}$$

where

$$k_n = 2\int_0^1 (1-Z^2)^{1-n}\quad dz$$

Values of k^n for various values of n are given in Table I.

TABLE I

n =	0	0.25	0.5	0.75	1.0
k^n =	1.33	1.44	1.57	1.75	2.00

THE EFFECT OF AMPLITUDE ON MODULUS

Value of n.—The value of n in Equation (2) is a measure of the nonlinearity of the system and can be obtained by a plot of log P against log d under isothermal conditions. Typical plots are given in Figure 6. It should be noted that n may be temperature dependent.

TABLE II

Sample	n from (ref. 8)	n determined on power loss machine
Natural gum stock	0	0.09
Krylene gum stock	0	0.15
Vulkollan gum stock	0	—
Natural rubber + 20 parts black	0.12	—
Natural rubber + 50 parts black	0.25	0.4
	0.33	—
Butyl 50 parts black	0.53	0.60
SBR 50 parts black	0.25	0.28
Neoprene 50 parts black	—	0.25
Hycar 50 parts black	—	0.26
Reclaim compounds	—	0.20
	(ref. 9)	
Natural ruber gum stock	0	0.09
Copolymer gum stock	0	—
N.R. + 50 parts black	0.23	0.4
	(ref. 7)	
N.R. + 60 lamp black	0.14	—

The same phenomenon has been noted by Meij and Amerongen[8], Fletcher and Gent[9], and McCallion and Davies[7] and in Table II values of n derived from their results are given and are in reasonable agreement with results on this machine.

The deflection is measured when the sample is rotating, since the value of dynamic modulus can then be obtained from Equation (2), and errors due to flow under static load are avoided.

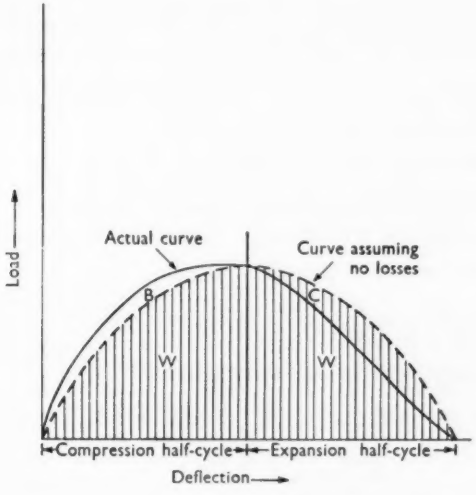


FIG. 7.

Stored energy.—The energy stored in the sample is found as follows: The work done in compressing the element to its maximum deflection d is

$$dW = \frac{EFbdx}{h^{1-n}} \int_0^d y^{1-n}\, dy = \frac{FEbdx \cdot d^{2-n}}{h^{1-n}\,(2-n)}$$

The number of elements which pass point B (Figure 7) in one revolution is $2\pi r/dx$.

$$\therefore \text{Work done per revolution} = W = \frac{FEb2\pi \cdot rd^{2-n}}{h^{1-n}\,(2-n)}$$

From Equation (2), $\dfrac{FEb}{h^{1-n}} = \dfrac{P}{\sqrt{r}\, d^{\frac{1}{2}-n} \cdot k^n}$

$$\therefore \text{Work done per revolution} = \frac{P\,2r}{k_n \sqrt{r}\, d^{\frac{1}{2}-n}} \cdot \frac{d^{2-n}}{2-n}$$

Or

$$W = \frac{2\pi}{(2-n) \cdot k_n} \sqrt{r}\, P \sqrt{d} = C_n P \sqrt{d}\ \text{Joules} \qquad (4)$$

The values of C_n for various values of n are given in Table III.

TABLE 3

n	C_n
0	0.165
0.25	0.174
0.5	0.186
0.75	0.201
1	0.220

Calculation of resilience.—W is not the total energy input to the system but is the value of the energy stored at the maximum deflection since there has been energy loss in reaching that deflection. This is shown in Figure 7.

It is assumed that the resilience value is the same during the compression and expansion parts of the cycle, i.e., resilience expressed as a ratio is independent of the actual value of the energy involved in the cycle, so that a value of resilience for the whole cycle can be calculated.

Let the total energy input/revolution = A
Let energy lost during compression/revolution = B
Let energy lost during expansion/revolution = C
Let total energy loss/revolution = L

$\therefore L = B + C$ and $W = A - B$

Then $\dfrac{B}{A} = \dfrac{C}{A-B} = \dfrac{C}{W}$

where W = energy stored at maximum deflection

$$\therefore \frac{A-W}{A} = \frac{L-B}{W} = \frac{L-A+W}{W}$$

$$\therefore \frac{W}{A} = \frac{A-L}{W}$$

Resilience $R = 1 - \frac{L}{A}$ by definition

Eliminating A from these two expressions gives:

$$\sqrt{R} = -\frac{L}{2W} + \sqrt{1 + (L/2W)^2} \tag{5}$$

This gives the resilience R as a function of L/W, where L is the measured loss and W is calculated from Equation (3) from measurements of P and d. Hence the resilience can be determined when L/W has been calculated. Tables are compiled giving the value of R for values of L/W.

COMPARISONS WITH OTHER DERIVATIONS OF MODULUS, AND LOSS OF A ROLLING WHEEL

(*a*) *Application to the case of a tire running on a flat surface.*—Evans[1] has calculated the rolling resistance and load-deflection characteristics of a solid tire rolling on a flat surface. Using our nomenclature, he derives the equation,

$$P = \frac{8\sqrt{2}}{3} E \frac{b}{h} \sqrt{r}\, a^{\frac{3}{2}}$$

for the relationship between load and deflection, in which a, the deflection on a flat surface, corresponds to $\frac{d}{2}$ for our case of when the wheel runs on a surface of equal curvature.

For the case where $F = 1$ and $n = 0$ (i.e. the case he considers since he does not deal with form factor or the modulus dependence on amplitude) our Equation (2) becomes,

since $k_n = \frac{4}{3}$,

$$P = \frac{4}{3} E \frac{b}{h} \sqrt{r}\, d^{\frac{3}{2}}$$

substituting $d = 2a$

$$P = \frac{8}{3} \sqrt{2}\, E \frac{b}{h} \sqrt{r}\, a^{\frac{3}{2}}$$

which is identical with his equation.

In considering the rolling resistance of a tire, Evans expresses this as the fraction h of the energy input to the tire which he expresses as $p_0 u$ where p_0 is the average load and u the deflection, so that the unit loss $L = h p_0 u$.

However, the product $p_0 u$ is the energy stored at maximum deflection and not the total work input since the losses involved in attaining the deflection are neglected.

Consequently, his value h corresponds to our value L/W and not to the resilience R as defined.

(*b*) *With an apparatus similar in principle.*—Since this paper was read, our

attention has been drawn to a machine similar in design described in a paper by M. M. Resnikovski, Vostroknutov and Khromov[10].

In the machine the rubber is deformed by a roller of much smaller radius than that of the sample and a formula for the dynamic modulus (using our terminology) is given as

$$E = \tfrac{3}{4} \frac{Ph^2 \sqrt{\tfrac{1}{2}\,(1/r + 1/r)}}{bd^{\frac{1}{2}} r \log r/r_1}$$

since $r - r_1 = h$ and

$$\log \frac{r}{r_1} = -\log\left(1 - \frac{h}{r}\right)$$

$$= \frac{h}{r} \text{ to the first approximation.}$$

The expression reduces to,

$$E = \frac{3\,Ph}{4b\,d^{\frac{1}{2}}\sqrt{r}}$$

which is identical with Equation (3) when $F = 1$, $n = 0$, $k_n = \frac{4}{3}$. These authors, however, do not consider resilience, but only the measured loss and loss modulus.

(c) *Case of a rigid wheel rolling on a flat rubber surface.*—This case has been considered by Tabor[2] who showed that the rolling resistance experienced by the wheel could be entirely accounted for by hysteresis losses (as determined by a separate experiment) in the rubber. This confirms our assumption that the drag exerted on the rotating drum by the rubber sample can be used to calculate the rubber resilience.

Discussions on errors and corrections to be applied.—The mathematical treatment given above for the calculation of energy input is subject to certain approximations.

(1) *Shape of the deformed sample.*—Errors arise from the assumption that the deformation of the rubber is geometrically identical with the segment of the steel drum indenting the sample. In practice the rubber at the point of initial contact with the drum follows a smooth curve in place of the mathematical discontinuity at the junction of intersecting circumferences.

This has been discussed for discs on a rigid core by Simpson[11] and numerical solutions have been obtained to selected problems. Errors arising from this will be small and will be included in the experimentally determined form factor.

(2) *Form Factor.*—The load-deflection relationship of compressed rubber will vary according to the ratio of the dimensions and end constraints imposed on the sample.

In order to obtain a general value E of modulus independent of the sample used a correcting factor known as the Form Factor or Shape Factor[12,13] is used to obtain the true modulus from the measured modulus. This is an empirical factor normally found by an experiment comparing the modulus of the experimental sample with the value obtained from a cylinder of unit height and diameter with the ends free.

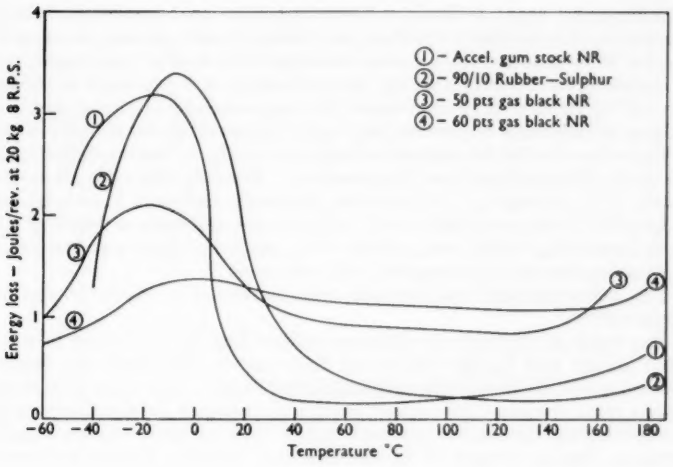


FIG. 8.

In our determinations, the moduli determined on the machine were compared with the values obtained on cylinders of the same materials on a Davies machine.

The average experimental value for the form factor for the wheel is 1.3 but a wide range of compounds should be examined.

(3) *Mathematical approximation.*—It is assumed that the length h_0 of the element is constant and equal to the radial distance h throughout the deformation cycle. The error due to this is assessed below.

Substituting $h = h_0\left(1 + \frac{d - y}{2r}\right)$ in Equation (2) and since $\bar{y} = \frac{2}{3}d$.

$$\therefore \quad h = h_0\left(1 + \frac{d}{6r}\right)$$

Equation (2) becomes

$$P = \frac{FEb}{h_0^{1-n}}\, r\, d^{\frac{1}{2}-n}\, k_n\left(1 - \frac{d}{6r}\right)$$

Since $\frac{d}{6r}$ is less than 0.015 for the deflection used, the errors are normally less than 1 per cent, and can be ignored both for modulus and resilience calculation.

RESULTS

The information obtained from the machine is in the form of energy loss in joules per revolution and of sample deflection under known loads.

Typical examples of these values are plotted against temperature in Figures 8 and 9.

While these data are of value for comparative purposes between different compounds, it is necessary to obtain the values of resilience and modulus if the data are to be used for more general investigations and for design purposes.

For modulus and stored energy determinations it is necessary to obtain the value of the index n in the expression for the load-deflection relationship since modulus is amplitude dependent and n gives a parameter for this dependence.

The value of n can be determined experimentally by taking deflection readings under different loads and temperatures. Possibly, after the accumulation of data over a range of compounded materials, sufficient knowledge of the variation of n with composition will be known for appropriate values of n to be selected according to the composition of the particular sample and so avoid the need for experimental determination in each case.

The deflection-load readings are then converted to modulus and stored energy values.

The value of resilience is obtained by dividing the measured loss by the stored energy and finally converting this ratio to the resilience value. In practice, tables are prepared relating deflection-load and n value with modulus, and the ratio of energy loss/stored energy to resilience for rapid conversion of the experimental data to the required forms. The results in Figures 8 and 9 are plotted in Figures 10 and 11 as modulus and resilience against temperature; further results of modulus and resilience for different types of polymer and compounds are given in Figures 12 and 13.

Comparison with pendulum resilience values.—The 50° C values can be compared to results obtained on the same compounds tested on the Healey rebound pendulum[3].

Table IV shows substantial identity of values between the two instruments, the slightly lower values on the power loss machine being due to its effective frequency being approximately twice that of the pendulum and the correspond-

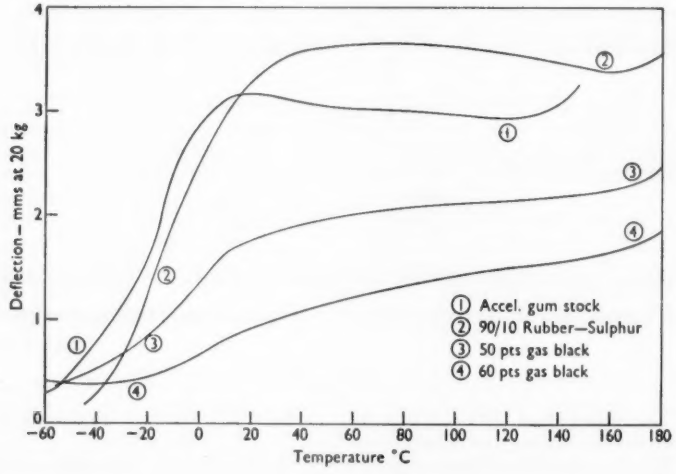


FIG. 9.

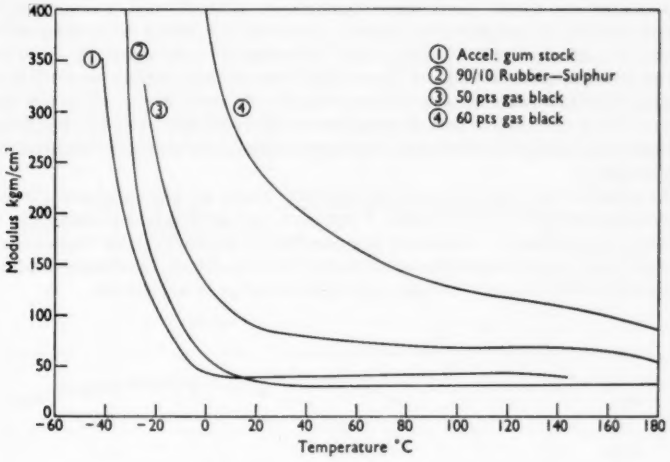


FIG. 10.

ing reduction in resilience being approximately 0.03. In each case the values are substantially independent of amplitude.

Effect of amplitude on resilience.—McCallion and Davies[7] have shown that the resilience of natural rubber compounded stocks increases appreciably as amplitude decreases but that at amplitudes above 5 to 10 per cent the resilience approximates to a steady value.

TABLE 4

Compound	Power loss machine		Pendulum	
		Ave		*Ave*
Butyl tread	a. 41		d. 41	
	b. 39	41	e. 41	41
	c. 40		f. 41	
PVC	a. 53		d. 50	
	b. 52	52	e. 52	52
	c. 51		f. 55	
Krynol tread	a. 57		d. 59	
	b. 57	57	e. 59	59
	c. 56		f. 60	
N.R. tread	a. 71		d. 73	
	b. 70	70	e. 74	74
	c. 70		f. 75	
N.R. sidewall	a. 78		d. 82	
	b. 76	76	e. 81	82
	c. 74		f. 82	
N.R. gumstock	a. 89		d. 91	
	b. 88	88	e. 91	91
	c. 87		f. 90	

a. b. c. Resilience values at 13, 10 and 7 per cent deflection, respectively.
d. e. f. Pendulum values at Large, Medium and Small deflection (approx. equal a. b. c.).

Fletcher and Gent[9] show that resilience of natural rubber compounds increases rapidly at amplitudes below 3 per cent, the effect increasing with increase in carbon content. Meij and Amerongen[8] also show an increase in resilience at amplitudes below 2 per cent for natural rubber and SBR compounds, but that butyl stocks decrease rapidly in resilience at these low amplitudes. They also show that at amplitudes above 2 per cent the resilience of all compounded stocks decreases but approximates to a steady value at higher amplitudes.

The power loss machine results and also those on the pendulum were obtained at amplitudes greater than 5 per cent and so will be substantially independent of amplitude. However, the amplitude dependence of resilience could be important in products operating under low amplitude conditions and measurements should be made over an appropriate range of amplitude.

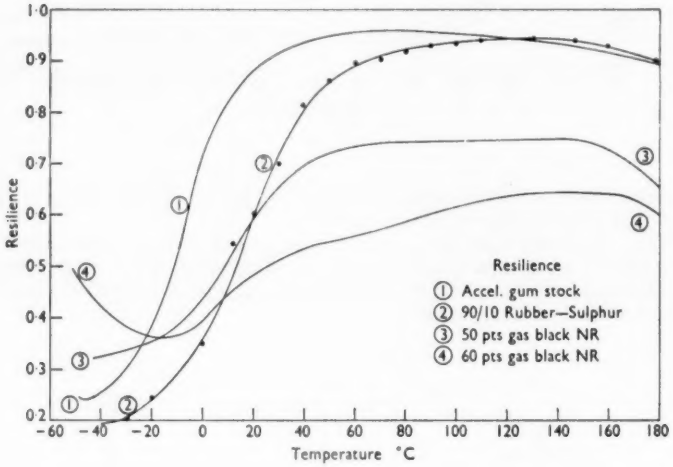


FIG. 11.

The effect of amplitude on modulus.—The index n in the modulus formula relates modulus to strain amplitude.

The value of n is near zero for uncompounded rubbers, and consequently these do not change in modulus with amplitude. However, n has values up to 0.5 for compounded materials. For tread compounds the value of 0.3 to 0.5 for n means that a 10:1 change in amplitude will result in an effective modulus change by two to three times.

One mechanism of the reduction in modulus of filled rubbers appears to be breakdown of the structure of the filler which, as Fletcher and Gent[9] have shown, recovers after a rest period but it should be noted that the modulus of an SBR gumstock is amplitude dependent so that the cause does not lie solely in the filler.

Effect of frequency on resilience and modulus.—Because of viscoelastic properties of rubber, the resilience should decrease and the dynamic modulus in-

crease with increase in frequency. Values obtained over a frequency range of 100 to 3000 cps on a variable frequency machine similar to the machine described, are given in Figure 14 for natural rubber gumstocks, lamp black stocks and some thiokols. The experimental results are of the form expected.

While this effect is of practical significance if widely different frequencies are involved it is small compared with variation in the properties due to temperature changes and can be obtained by use of the Ferry-Williams transform.

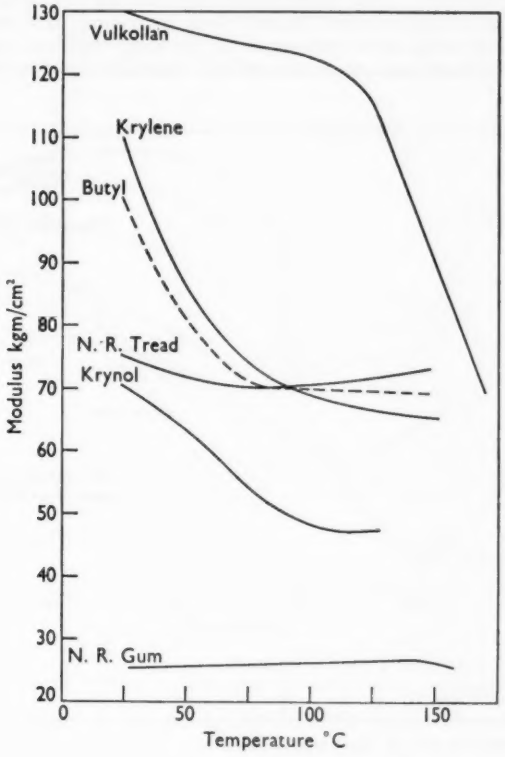


FIG. 12.

Effect of temperature on resilience.—The resilience of compounds depends on their temperature and above a temperature near the second order transition temperature rises rapidly with increase in temperature to a temperature invariant value. Over the temperature range from 0° to 100° C, the activation energy for high amplitude deformations is 10 to 12 kcal for gum stocks indicating that the loss mechanism arises from the relative movement of molecular chains since a similar value of activation energy is obtained from rheological experiments on unvulcanized rubbers. However, if temperature is increased further it will

be found that resilience decreases and examples are given in Figures 11 and 13 and in Figure 15 in which two solid tire compounds are compared.

This phenomenon is of an irreversible nature and a compound, on subsequent temperature cycles, will follow approximately the cooling curve of the previous cycle. This has the effect of a permanent reduction of the maximum resilience obtainable coupled with a shift to higher values of the critical temperature.

Data given in Figure 16 shows that the critical temperature increases with decrease in resilience. This phenomenon depends on the compounding ingredients involved, for example, channel black compounds give lower temperature values than lamp black compounds of the same resilience value. In the case of high resilience gum stocks the critical temperature can be below 100° C.

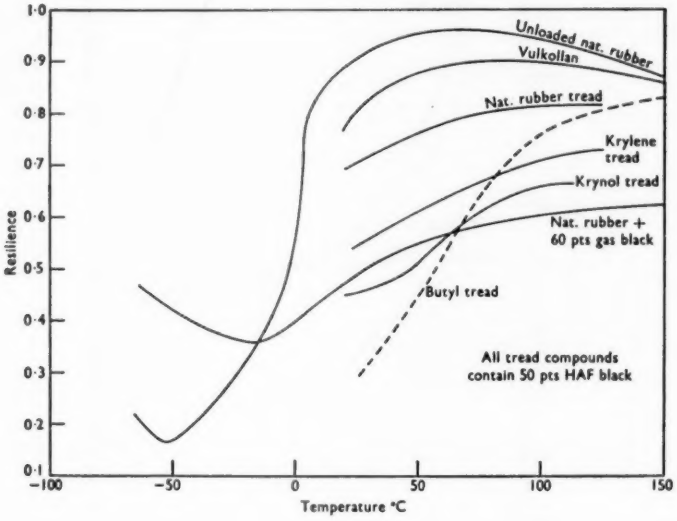


FIG. 13.

This phenomenon is obviously of considerable practical importance in designing compounds for use at high temperatures.

Use of resilience-modulus data.—As a practical example of the value of obtaining resilience, modulus and power loss data over a range of temperatures, Figures 15 and 17 give data on two solid tire compounds, for which the energy loss at 50° C under constant load conditions is identical. It will be seen, however, that although compound B gives a rather lower loss than A between 50° and 120° C, it then passes its critical temperature, and a runaway increase in temperature will result at temperatures above 120° C.

The higher modulus of compound B compared with A will result in less cushioning by solid tires made from this compound.

The full examination of the test results on these two compounds illustrates that knowledge of the modulus, resilience, energy loss under constant load

conditions and the critical temperature enables a useful forecast of their behavior under defined conditions to be made.

If the operating conditions are altered to constant deflection instead of constant load there will be appreciably higher energy loss in the harder compound B than in A and the calculated value is shown in Figure 17.

In the case of a pneumatic tire the situation is more complex than in solid tires since energy loss takes place both due to bending of the tread, and sidewall

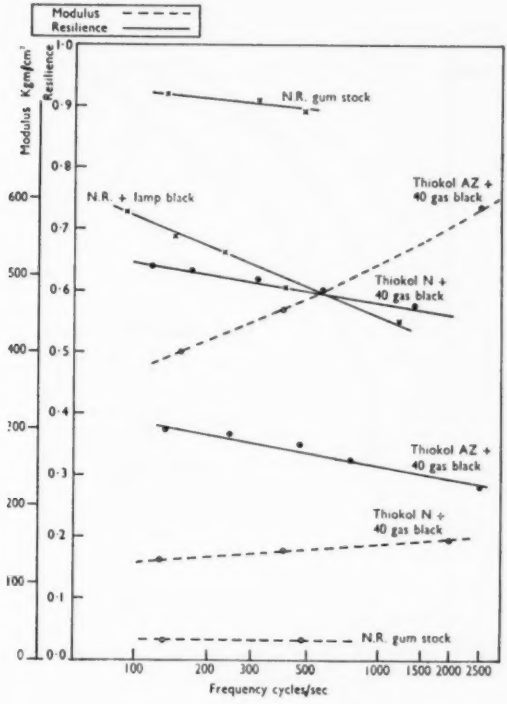


FIG. 14.

and case and also due to compression of the tread and casing under the constant load per unit area provided by the inflation pressure. Since a tire is designed to operate at a constant deflection under different loads by change of inflation pressure it is evident that the calculation of its energy losses under differing conditions is a matter of considerable complexity.

By obtaining data from the machine and calculating losses for both constant load and constant deflection conditions an approach can be made to this problem.

CONCLUSIONS

The machine described provides an easy method of measuring the resilience, modulus and power loss of rubber over a range of temperatures and at various amplitudes of deflection—both of which factors affect the dynamic properties of rubber.

The transcribing of laboratory results on compounds to rolling resistance and temperature rise in tires involves knowledge of their working conditions as well as the dynamic properties of the polymers.

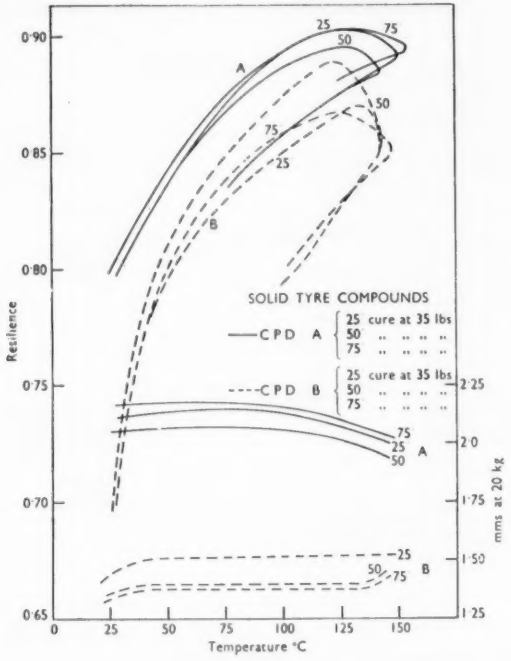


FIG. 15.

SUMMARY

The energy loss in rubber depends on its resilience and modulus and the operating conditions of the product.

The Rotary Power Loss machine enables these properties and the energy loss in the sample under both constant load and constant deflection conditions to be measured.

A wheel-like rubber sample is deflected against a rotating drum and the energy loss is measured directly.

The energy stored in the deflected segment of the sample is computed from the load and deflection. The resilience calculation takes account of the energy loss occurring during deflection of the sample.

Experimental results show that the modulus of most rubbers depends on the amplitude of deformation and the mathematical treatment uses a relationship of the form $E = E_0(S^{-n})$ which agrees substantially with the experimental results. The value of "n" is regarded as one of the parameters defining the properties of the rubber.

The paper includes experimental results over a wide range of tempera-

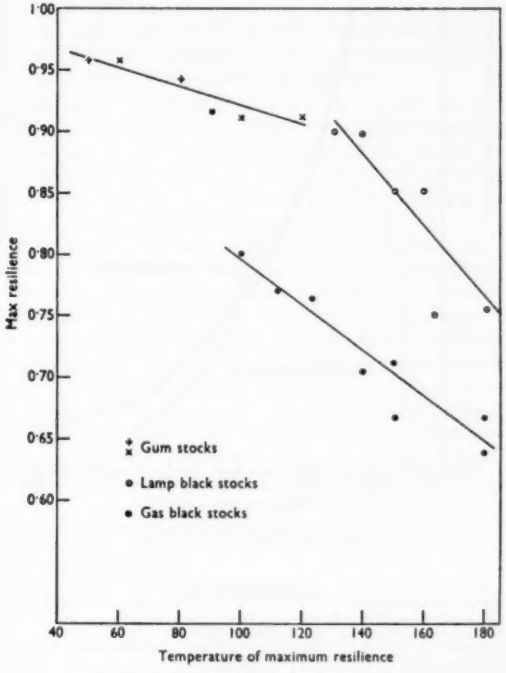


FIG. 16.

tures and these show that resilience may decrease irreversibly at high temperatures.

The instrument is designed as a robust instrument which can be operated in a routine test laboratory.

ACKNOWLEDGMENTS

The authors express their thanks to the Directors of the Dunlop Rubber Co. Ltd., in whose laboratories the work was carried out and to the members of the staff who have assisted in the construction of the machine and its operation.

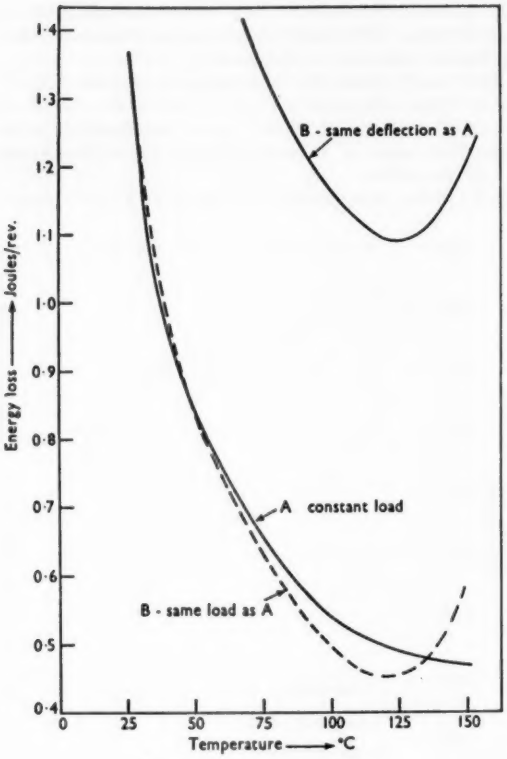


FIG. 17.—Solid tire compounds.

REFERENCES

[1] Evans, I., *Brit. J. Appl. Phys.* **5**, No. 5 187 (1954).
[2] Tabor, D., *J. Am. Soc. Lub. Engrs.* **12**, No. 6, 379 (1956).
[3] Jones, F. B., and Pearce, W. H., *Proc. Rubber Technol. Conf.*, London, **1938**, p. 830.
[4] Waring, J. R. S., *Trans. Inst. Rubber Ind.* **26**, 4 (1950).
[5] Fletcher, W. P., and Gent, A. N., *Trans. Inst. Rubber Ind.* **26**, 45 (1950).
[6] Roelig, H., *Proc. Rubber Technol. Conf.*, London, **1938**, p. 821.
[7] McCallion, H., and Davies, D. M., *Proc. Inst. Mech. Engrs.* London, **169**, No. 57 (1955).
[8] Meij, S. de, and Amerongen, G. J. van, "Dynamisch–Mechanische Eigenschaften von Kautschukmischungen." Deutsche-Kautschuk Gesellschaft. Munich Conference, 21st-23rd October, 1954.
[9] Fletcher, W. P., and Gent, A. N., *Trans. Inst. Rubber Ind.* **29**, 266 (1953).
[10] Resnikovski, Vostroknutov, and Khromov, *Starenie i Utomlenie* **1953**, 68.
[11] Simpson, M. G., Ph.D. Thesis, London, 1955.
[12] "Rubber in Engineering—The Services Rubber Investigations", 1945, p. 204.
[13] Jenkins, H. L., and Cooper, D. H., *Proc. Second Rubber Technol. Conf.*, London, **1948**, p. 214.

DISCUSSION

Mr. J. H. HARDMAN—Mr. Bulgin mentioned that good correlation had been obtained between the small samples on the test machine and full scale solid tires. Could he tell us whether, by any mathematical formulas, he could relate the test results to pneumatic tires.

Mr. BULGIN, in reply, said that the correlation with the rolling resistance of solid tires rests upon the publication by Evans, referred to in the paper. We have shown that his derivation of the energy input to the solid tire is in agreement with the one we use for our samples which are tested under solid tire conditions.

In the case of pneumatic tires the derivation of energy input is more complex than for solid tires since a portion of the energy is stored by bending the tread and sidewall and the remainder in compressing the casing and tread on the road under the inflation pressure in the tire. Neither of these components correspond to the solid tire conditions and the situation is complicated by the fact that one will decrease and the other increase with change in modulus. It is probably possible to derive a formula for the rolling resistance of pneumatic tires from these principles in conjunction with experimental determinations of modulus of the cord-rubber structure and its resilience.

Mr. E. W. MADGE said that this work had been carried out for many years and in its first stages was associated with a compounding study with natural rubber on this machine. It had a particular value at the present time since the synthetic rubbers differ so very muc in their characteristics from natural rubber, particularly in heat build-up. This type of paper relating to new tests and new machines was of particular importance at this time.

Mr. J. W. DENSON said that he would like to congratulate Mr. Bulgin and Mr. Hubbard on an excellent paper and also to say how much he agreed on the importance of measuring resilience over what is normally their working range of temperature, rather than the stock room temperature conditions in which we measured in the past. For that reason he thought this type of machine which lends itself to relatively easy measurement of resilience at a range of temperatures and resiliences is a very important contribution. There were two points he would like to mention: resilience can be measured under three conditions of constant load, constant deformation and constant work. He gathered that the authors did most of the work under conditions of constant load. Had any work been done on conditions of constant deformation as it would be quite simple to work it under these conditions? Would it be possible to work it under all three of these conditions just by altering the method of operation? Could Mr. Bulgin comment on the question of temperature build-up when the frequency is altered?

Mr. BULGIN replied that whereas it is possible to operate the machine under selected conditions of constant load or constant deflection or even constant loss, the aim is to calculate from the readings obtained, the resilience and modulus values over the appropraite temperature, frequency and amplitude range. It is then possible to apply this to any known operating conditions of the product.

The principal effect of change of frequency will be to increase the work input proportionally to the frequency. There may also be small changes in energy loss since the value of resilience decreases slightly while the modulus increases with increasing frequency.

Mr. F. B. JONES asked whether Mr. Bulgin would enlarge on the question of critical temperature? Could he give the critical temperatures for a variety of compounds?

Mr. BULGIN answered that resilience increases between sub-zero temperatures and the critical temperature of a compound so that any increase in temperature due to any internal or external cause increases the resilience and

decreases the loss and so enables stability to be re-established at a new temperature.

However, above the critical temperature the loss increases instead of decreasing and so the situation becomes unstable and a rapid increase of temperature results and could cause the destruction of the product.

The critical temperature is inversely related to resilience so that the practical anomaly exists that a compound with a very high resilience, say at 50° C, may be less suitable for use at high temperatures than a compound with a rather lower resilience at 50° C. This emphasizes the importance of measuring resilience over the whole range of working temperature.

If the compound is heated above the critical temperature a permanent reduction in resilience occurs and subsequent measurement of resilience with temperature will show a lower maximum resilience which, however, occurs at a higher critical temperature. In this way, providing the temperature does not rise to a destructively high level at any time, a compound will tend to stabilize itself with successive temperature cycles if the final working temperature is below the new critical temperature.

The data in Figure 16 summarizes the known position of critical temperature with compounding but there is scope for determination of this value with detailed variation of compound.

Dr. D. G. MARSHALL said he felt that such an eloquent exposition of dynamic testing must have struck terror into those accustomed to compound on rebound resilience. He wondered whether some of the results indicated in the lecture threw some ray of hope on this situation, in that some of the objectionable parameters such as the temperature dependence of modulus and also the amplitude dependence of modulus seemed to depend on resilience. Possibly resilience alone may not be as misleading as one had at first sight thought.

Mr. BULGIN replied that the energy loss in a product will be that given by the fraction (1 − resilience) of the "work input" which in turn depends on the modulus of the compound.

There are thus a number of independent variables which determine energy loss; for example, the resilience and modulus of the compound and the conditions of use of the product. The resilience and modulus are equally important properties and their value should be known over the full operating temperature range.

Certain of the second order effects such as the amplitude dependence of modulus and critical temperature phenomena are of considerable practical significance and do appear to be related in certain ways to resilience. Since these relationships are not accurately known at present, it is desirable that measurements should be made, since the existing data indicate that these properties may depend on the compound formulation.

Mr. A. R. PAYNE said that the major effect of amplitude had been stressed in the paper. This amplitude effect was a bugbear in the majority of testing that had been done to date. This point must be stressed, because there have been many attempts to try to correlate different instruments, and the differences all go back in the end to the fact that the amplitude conditions have not been specified, and the amplitude effect has been ignored. We just could not ignore the amplitude effect for we saw a decrease in modulus of a factor of 3 or 4 or more to 1 for a 40-part loaded carbon black vulcanizate. Another point was that in doing the sort of test described we would be approximating to the conditions in which we used rubber in mountings and in tires, so the sort of information we got from a test of this sort was far more informative than, say, a meas-

urement of tensile strength, a test far removed from service conditions, so any machine that gave us some answer or results nearer to the actual service conditions was to be greatly appreciated. We had also a machine which could be used by nonskilled personnel. He knew that laboratory dynamic tests required a great deal of electronics and required skilled personnel to use them, but we had here apparently a machine which gave results similar to that obtained from much more complex dynamic testing machines using unskilled personnel to perform the experiments. He wished to ask, in making the tests described, whether one started at the lowest amplitude and then worked up in amplitude or *vice versa*, as the previous history had an appreciable effect on the results? In plotting the results aginst temperature, was this the ambient temperature of the temperature inside the rubber that was plotted; for, if inside, it was going to be an enormous temperature.

Mr. BULGIN replied that the temperature is measured inside the sample by a thermocouple passed through it so that it approximates to rubber temperature; the steel center is somewhat cooler than the rubber but measurement with a thermocouple indicates that the variation within the rubber itself is small.

The important problems raised by the amplitude dependence of modulus came to our notice as the result of observations made on the machine and so far the majority of results have been obtained under approximately constant load conditions.

When the deflection observations have been made by altering the load, the operation was carried out at a series of isothermal conditions so that in effect some readings were obtained before, and some after, high amplitude deformations.

We did not observe any systematic changes during this procedure but a closer examination may, of course, reveal them.

Mr. B. J. A. MARTIN said that in going back to the rolling resistance of pneumatic tires it was a general observation that if the resilience of a tread compound was reduced, the rolling resistance of the tire increased; he asked how far are we likely to be misled in using this machine for designing pneumatic tire tread compound, or in another form, what special precautions should be observed in the test procedure in order to get correct relative values?

Mr. BULGIN answered that in the case of pneumatic tires it is customary to compound the casing and tread stocks to more or less fixed values of modulus and consequently it is true that an increase of resilience results in lower energy loss and rolling resistance. Since, however, modulus has a similar level of significance to resilience if the modulus is altered the energy loss will also alter, consequently in tires it is necessary to control both properties in order to obtain the optimum compound and this becomes increasingly important with the change from natural to synthetic rubbers.

In this paper we place equal stress on obtaining and using both these measurements and the machine is specifically designed to give them.

Mr. F. E. SMITH asked whether any difficulty arose from the fact that different samples under test will have different coefficients of friction against the steel pulley?

Mr. BULGIN replied that he had not observed any effects due to coefficients of friction. The sample, although deformed, runs at the speed of the drum within an error of $\pm$ 1 per cent. This is rather surprising since the sample is under considerable deflection, but it does appear that there is no differential slip between the sample and the steel drum and the speed of the sample perimeter is that of the drum.

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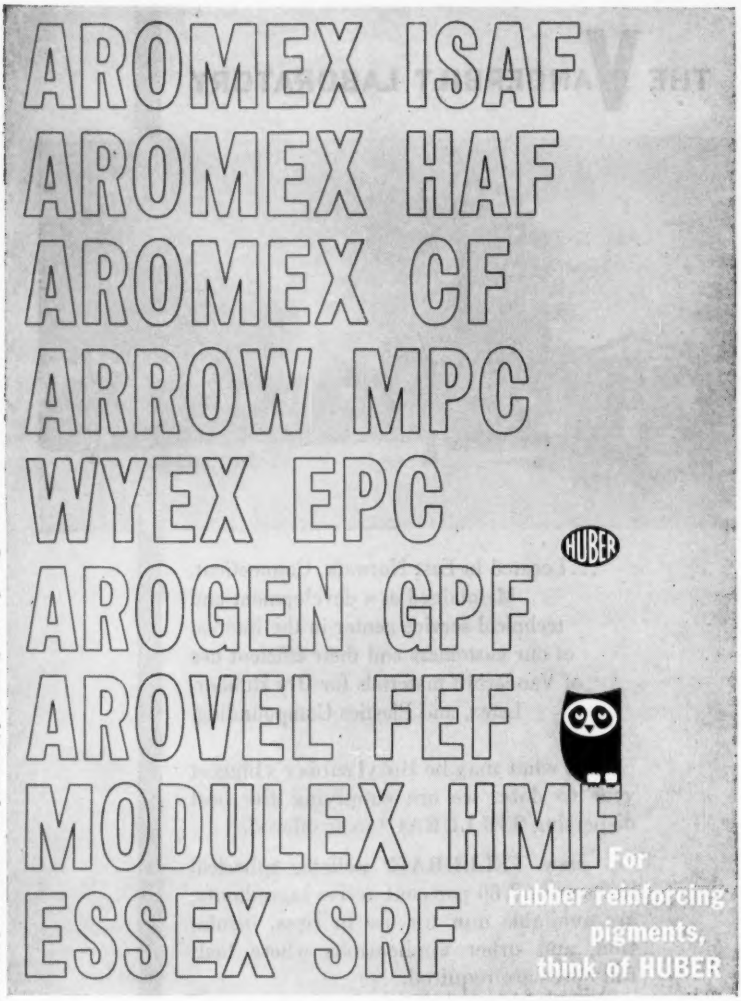
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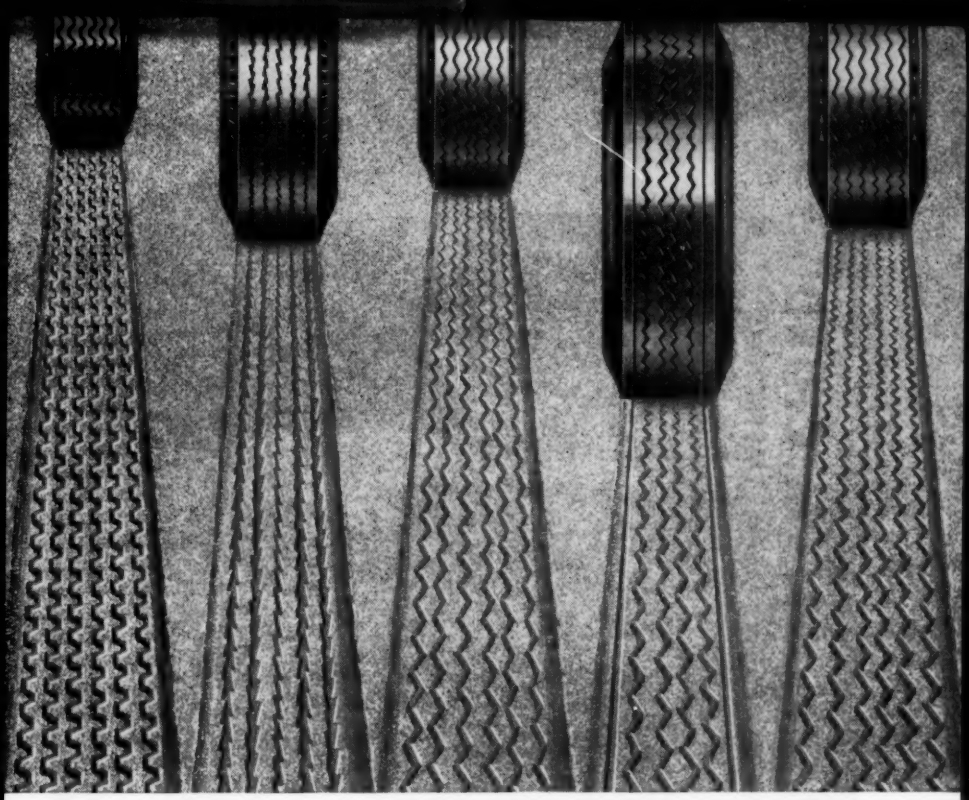
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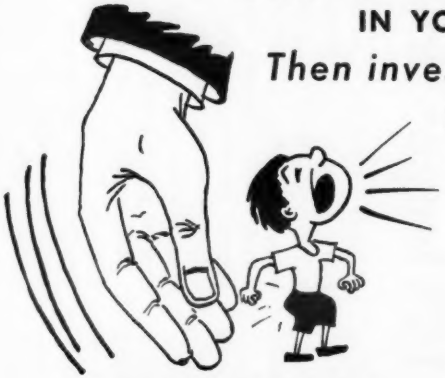
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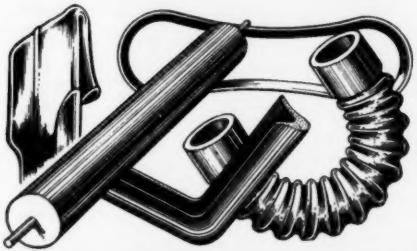
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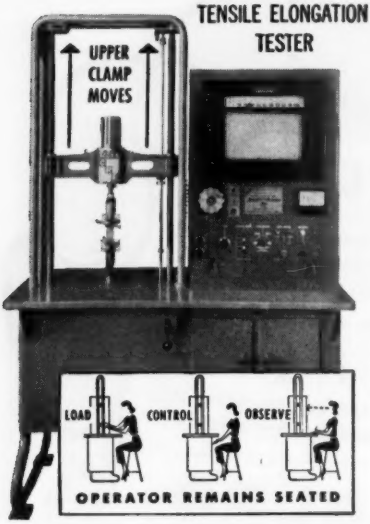
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